Electronic Supplementary Material (ESI) for Chemical Communications

Highly Diastereo- and Enantioselective [3+2] Annulation of Isatin-derived Morita-Baylis-Hillman Carbonates with Trifluoropyruvate Catalyzed byTertiary Amine

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1. General Method

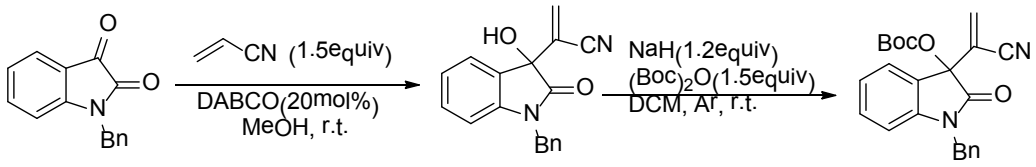
All reactions were carried out in oven dried flasks. All the ^{1}H and ^{13}C NMR were recorded on Bruker-AV 300 spectrometer and chemical shifts reported in $CDCl_3$ or DMSO with tetramethylsilane as an internal standard. IR spectra were recorded on a NICOLET 6000 infrared spectrometer. Melting points were measured on Beijing-Tiker X-4 apparatus without correction. HRMS spectra were recorded on Thermo Fish Scientific-Exactivemass spectrometer. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. Common reagents were purchased from commercial sources and were used without further purification. Cinchona alkaloid-type catalysts[1] and all the substrates[2]wereprepared according to original or modified literature procedures. In each case, enantiomeric ratio was determined by chiral HPLC analysis on Chiralcel column in comparison with authentic racemates. Optical rotation data was examined in $CHCl_3$solutionand are reported as follows: $[\alpha]_D^{rt}$ (*c* in g per 100 mL of solvent). Column chromatography was performed using silica gel (200-300mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates.

References:

(1) Waldmann, H.; Khedkar, V.; Duckert, H.; Schrmann, M. Oppel, I. M.; Kumar, K. *Angew. Chem. Int. Ed*. **2008**, *47*, 6869.

(2)(a)Aikawa,K.; Mimura,S.; Numata,Y.; Mikami, K. Eur. *J. Org. Chem.***2011**, 62–65. (b)Shanmugam,P.;Vaithyganathan,V.;*Can. J. Chem.***2009**, *87,* 591.(c) Štambaský,J.; Malkov,A. ;Kočovský,V. P. *J. Org. Chem.***2008**, *73*, 9148.

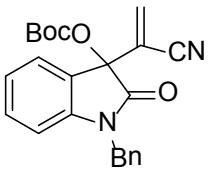
2 General procedurefor preparation of Isatin-derived MBH carbonates



A mixture of *N*-benzyl isatin(6.2mmol, 1g), vinyl cyanide (9.3mmol, 0.61ml), and DABCO (1.24mmol, 139mg) in MeOH was stirred at room temperature. After completion of the reaction (monitored by TLC), the mixture was concentrated by vacuum, then was added EtOAc. The organic phase was washed with dilute hydrochloric acid and water. The organic layer was separated, dried (Na_2SO_4), and concentrated by vacuum. The crude product was purified by column chromatography over silica gel (gradient: petroleum ether / EtOAc = 4:1) to afford *N*-benzyl isatin-derived MBH adduct.

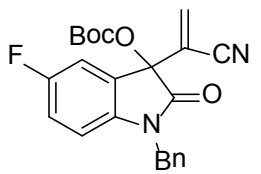
N-benzyl isatin-derived MBH adduct (1.7mmol, 493mg), was added slowly to a suspension of sodium hydride (2.1mmol, 49mg) in dry DCM (15ml) at room temperature and the mixture was stirred for 10min.Then the resulting solution was addedslowly to a solution of Boc anhydride (2.55mmol, 540.6mg) in 2 mL dry DCM at room temperature and stirred at room temperature for overnight. The reaction mixture was directly filtered and the filtrate was concentrated by vacuum.The crude product was purified by column chromatography over silica gel (gradient: petroleum ether / EtOAc = 8: 1) to afford the desired *N*-benzyl isatin-derived MBH carbonate.

1-benzyl-3-(1-cyanovinyl)-2-oxoindolin-3-yl tert-butyl carbonate (1a)



white solid. m.p. 126-128℃.^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32-7.25 (m, 7H), 7.12-7.07 (t, *J* = 7.4Hz, 1H), 6.75-6.72 (d, *J*=7.8Hz, 1H), 6.27 (s, 1H), 6.20 (s, 1H), 5.08-5.02 (d, *J*=15.9Hz, 1H), 4.94-4.89 (d, *J* = 15.9Hz, 1H), 1.40 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.9, 150.0, 143.4, 135.0, 133.4, 131.2, 128.8, 127.8, 127.3, 124.6, 123.9, 123.6, 120.4, 115.1, 110.2, 84.5, 79.3, 44.6, 27.6. IR ν_{max} (KBr, film, cm^{-1}): 1736, 1605, 1469, 1297, 758. HRMS (ESI): calcd for $C_{23}H_{22}N_2O_4$ $[M+Na]^+$413.1472, found: 413.1470.

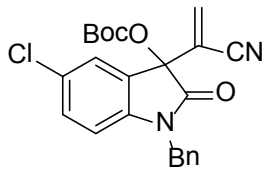
1-benzyl-3-(1-cyanovinyl)-5-fluoro-2-oxoindolin-3-yl tert-butyl carbonate (1b)



white solid. m.p. 152-154℃.^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.31-7.26 (m, 5H), 7.15-7.12 (dd, *J* = 7.5Hz, *J* = 2.7Hz, 1H), 7.01-6.95 (td, *J* = 9.0Hz, *J* = 2.7Hz, 1H),6.67-6.63 (dd, *J*=8.4Hz, *J*=3.9Hz, 1H), 6.34 (s, 1H), 6.25 (s, 1H), 5.06-5.00 (d, *J*=15.9Hz, 1H), 4.95-4.90 (d, *J* = 15.9Hz, 1H), 1.43 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.7, 159.4 (d, *J*=241.5Hz), 150.0, 139.3, 134.6, 133.7, 128.9, 127.9, 127.3, 126.1(d, *J*=8.5Hz), 119.8, 117.6 (d, *J*=23.3Hz), 114.8, 112.0 (d,

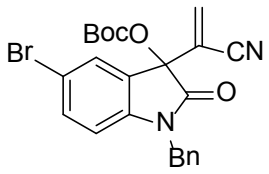
J=25.5Hz), 111.1 (d, *J*=8.3Hz), 84.8, 79.1, 44.7, 27.6. IR ν_{max} (KBr, film, cm^{-1}): 1743, 1606, 1496, 1262, 798. HRMS (ESI): calcd for $C_{23}H_{21}FN_2O_4$ $[M+Na]^+$431.1378, found: 431.1376.

1-benzyl-5-chloro-3-(1-cyanovinyl)-2-oxoindolin-3-yl tert-butyl carbonate (1c)



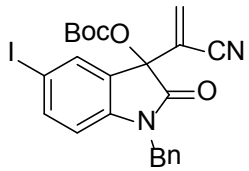
yellow solid. m.p. 146-148℃.^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.37-7.23 (m, 7H), 6.66-6.63 (d, *J*=8.4Hz, 1H), 6.34 (s, 1H), 6.25 (s, 1H), 5.04-4.99 (d, *J*=16.2Hz, 1H), 4.96-4.91 (d, *J* = 16.2Hz, 1H), 1.43 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.5, 150.0, 141.9, 134.5, 133.6, 131.2, 129.0, 128.9, 128.0, 127.3, 126.3, 124.2, 119.7, 114.8, 111.3, 84.9, 79.0, 44.7, 27.6. IR ν_{max} (KBr, film, cm^{-1}): 1745, 1614, 1485, 1263, 730. HRMS (ESI): calcd for $C_{23}H_{21}ClN_2O_4$ $[M+Na]^+$447.1082, found: 447.1080.

1-benzyl-5-bromo-3-(1-cyanovinyl)-2-oxoindolin-3-yl tert-butyl carbonate (1d)



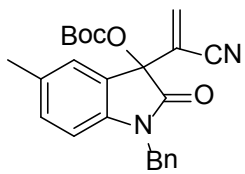
white solid. m.p. 147-149℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.48 (s, 1H), 7.41-7.28 (m, 6H), 6.61-6.59 (d, *J*=8.3Hz, 1H), 6.34 (s, 1H), 6.25 (s, 1H), 5.04-4.98 (d, *J*=15.9Hz, 1H), 4.96-4.91 (d, *J* = 15.9Hz, 1H), 1.43 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.4, 150.0, 142.4, 134.5, 134.1, 133.6, 128.9, 128.0, 127.3, 126.9, 126.6, 119.7, 116.2, 114.8, 111.8, 84.9, 78.9, 44.7, 27.6. IR ν_{max} (KBr, film, cm-1): 1746, 1611, 1484, 1293, 730. HRMS (ESI): calcd for $C_{23}H_{21}BrlN_2O_4$ $[M+Na]^+$ 491.0577, found: 491.0575.

1-benzyl-3-(1-cyanovinyl)-5-iodo-2-oxoindolin-3-yl tert-butyl carbonate (1e)



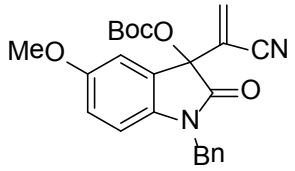
white solid. m.p. 145-147℃.^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.63-7.57 (t, 2H), 7.34-7.27 (m, 5H), 6.51-6.48 (d, *J*=8.2Hz, 1H), 6.33 (s, 1H), 6.24 (s, 1H), 5.03-4.98 (d, *J*=16.0Hz, 1H), 4.95-4.90 (d, *J* = 16.0Hz, 1H), 1.43 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$δ: 170.2, 150.0, 143.1, 140.0, 134.4, 133.5, 132.4, 128.9, 127.9, 127.3, 126.9, 119.8, 114.8, 112.3, 85.8, 84.9, 78.7, 44.6. 27.6. IR ν_{max} (KBr, film, cm^{-1}): 1746, 1605, 1482, 1296, 730. HRMS (ESI): calcd for $C_{23}H_{21}IN_2O_4$ $[M+Na]^+$539.0438, found: 539.0435.

1-benzyl-3-(1-cyanovinyl)-5-methyl-2-oxoindolin-3-yl tert-butyl carbonate(1f)



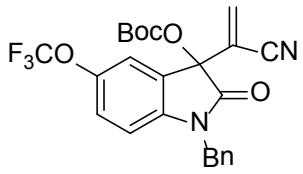
yellow solid. m.p. 162-164℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35-7.19 (m, 6H), 7.08-7.06 (d, *J* = 7.7Hz, 1H), 6.62-6.60 (d, *J*=7.6Hz, 1H), 6.28 (s, 1H), 6.20 (s, 1H), 5.05-4.99 (d, *J*=16.1Hz, 1H), 4.94-4.89 (d, *J* = 16.1Hz, 1H), 2.31 (s, 3H) 1.42 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.8, 150.0, 140.9, 135.1, 133.3, 133.2, 131.5, 128.8, 127.7, 127.3, 124.6, 124.5, 120.5, 115.2, 110.0, 84.4, 79.5, 44.6, 27.6, 21.1. IR ν_{max} (KBr, film, cm^{-1}): 1753, 1738, 1622, 1496, 1294, 730. HRMS (ESI): calcd for $C_{24}H_{24}N_2O_4$ $[M+Na]^+$ 427.1628, found: 427.1626.

1-benzyl-3-(1-cyanovinyl)-5-methoxy-2-oxoindolin-3-yl tert-butyl carbonate(1g)



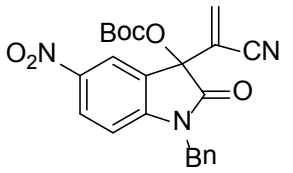
yellow solid. m.p. 114-116℃. 1H NMR (300 MHz, $CDCl_3$) δ: 7.37-7.28 (m, 5H), 6.99-6.98 (d, *J* = 2.3Hz, 1H), 6.81-6.77 (d, *J*=78.6Hz, *J*=2.3Hz 1H), 6.64-6.61 (d, *J* = 8.8Hz, 1H), 6.29 (s, 1H), 6.21 (s, 1H), 5.05-4.99 (d, *J*=15.9Hz, 1H), 4.93-4.88 (d, *J* = 15.9Hz, 1H), 3.75 (s, 3H), 1.42 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.6, 156.5, 150.0, 136.5, 135.1, 133.4, 128.8, 127.8, 127.3, 125.8, 120.4, 115.6, 115.1, 110.9, 110.9, 84.5, 79.6, 55.8, 44.6, 27.6. IR ν_{max} (KBr, film, cm^{-1}): 1757, 1724, 1606, 1497, 1287, 728. HRMS (ESI): calcd for $C_{24}H_{24}N_2O_5$ $[M+Na]^+$ 443.1577, found: 443.1575.

1-benzyl-3-(1-cyanovinyl)-2-oxo-5-(trifluoromethoxy)indolin-3-yl tert-butylcarbonate(1h)



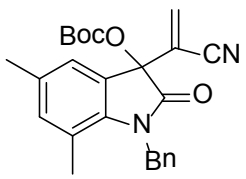
white solid. m.p. 103-105℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.36-7.27 (m, 6H), 7.17-7.13 (m, 1H), 6.73-6.71 (d, *J*=8.4Hz, 1H), 6.35 (s, 1H), 6.27 (s, 1H), 5.08-5.02 (d, *J*=15.9Hz, 1H), 4.94-4.89 (d, *J* = 15.9Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.7, 150.0, 145.2 (d, *J* =2.3Hz), 142.1, 134.4, 133.8, 129.0, 128.0, 127.3, 126.2, 124.3, 120.4 (d, *J* =255.8Hz), 119.6, 117.8, 114.7, 110.9, 85.0, 78.9, 44.8, 27.5. IR ν_{max} (KBr, film, cm^{-1}): 1745, 1623, 1491, 1454, 1264, 873. HRMS (ESI): calcd for $C_{24}H_{21}F_3N_2O_4$ $[M+Na]^+$ 497.1295, found: 497.1297.

1-benzyl-3-(1-cyanovinyl)-5-nitro-2-oxoindolin-3-yl tert-butyl carbonate(1i)



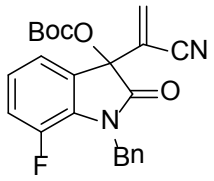
white solid. m.p. 133-135℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.26-8.23 (m, 2H), 7.37-7.31 (m, 5H), 6.84-6.81 (dd, *J* = 7.5Hz, *J* = 2.1Hz, 1H), 6.49 (s, 1H), 6.33 (s, 1H), 5.05 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.0, 150.1, 148.9, 144.0, 134.3, 133.8, 129.1, 128.3, 128.0, 125.7, 119.7, 118.8, 114.5, 110.2, 85.5, 78.4, 45.0, 27.6. IR ν_{max} (KBr, film, cm^{-1}): 1750, 1617, 1486, 1291, 735. HRMS (ESI): calcd for $C_{23}H_{21}N_3O_6$ $[M+Na]^+$ 458.1323, found: 458.1320.

1-benzyl-3-(1-cyanovinyl)-5,7-dimethyl-2-oxoindolin-3-yl tert-butyl carbonate(1j)



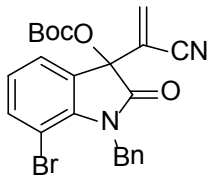
yellow solid. m.p. 160-162℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35-7.235 (m, 5H), 7.06 (s, 1H), 6.88 (s, 1H), 6.27 (s, 1H), 6.20 (s, 1H), 5.19(s, 2H), 2.28(s, 3H), 2.20(s, 3H), 1.43 (s, 9H). 13C NMR (75 MHz, $CDCl_3$) δ: 171.7, 150.1, 138.9, 137.3, 135.7, 133.3, 133.2, 128.8, 127.2, 125.9, 125.5, 122.3, 120.9, 120.5, 115.3, 84.3, 79.1, 45.8, 27.6, 20.7, 18.6. IR ν_{max} (KBr, film, cm^{-1}): 1744, 1727, 1605, 1499, 1288, 734. HRMS (ESI): calcd for $C_{25}H_{26}N_2O_4$ $[M+Na]^+$ 441.1785, found: 441.1782.

1-benzyl-3-(1-cyanovinyl)-7-fluoro-2-oxoindolin-3-yl tert-butyl carbonate(1k)



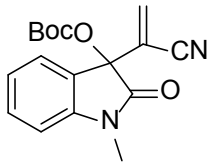
yellowsolid. m.p. 142-144℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41-7.24 (m, 5H), 7.21-7.18 (m, 1H), 7.12-7.04 (m, 2H), 6.22 (s, 1H), 6.20 (s, 1H), 5.10 (s, 2H), 1.41 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.6, 150.0, 147.6 (d, *J*=244.5Hz), 136.2, 133.8, 130.1(d, *J*=9.8Hz), 128.5, 127.7, 127.5, 127.5, 124.4 (d, *J*=6.0Hz), 119.9 (d, *J*=6.0Hz), 119.7 (d, *J*=6.0Hz), 119.4, 114.8, 84.8, 79.0, 46.1 (d, *J*=4.5Hz), 27.6. IR ν_{max} (KBr, film, cm^{-1}): 1754, 1631, 1476, 1286, 736. HRMS (ESI): calcd for $C_{23}H_{21}FN_2O_4$ $[M+Na]^+$ 431.1378, found: 431.1375.

1-benzyl-7-bromo-3-(1-cyanovinyl)-2-oxoindolin-3-yl tert-butyl carbonate(1l)



yellow solid. m.p. 161-163℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.50-7.47 (t, 1H), 7.38-7.36 (dd, *J* = 7.4Hz, *J* = 1.2Hz, 1H), 7.33-7.23 (m, 5H), 7.03-6.98 (dd, *J*=8.1Hz, *J*=7.5Hz, 1H), 6.24 (s, 1H), 6.22 (s, 1H), 5.52-5.46 (d, *J*=16.5Hz, 1H), 5.40-5.35 (d, *J* = 16.5Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.6, 150.0, 141.0, 137.2, 136.9, 133.9, 128.5, 127.0, 127.2, 126.4, 124.8, 122.9, 120.0, 114.9, 103.3, 84.9, 78.4, 45.4, 27.6. IR ν_{max} (KBr, film, cm^{-1}): 1747, 1604, 1463, 1289, 730. HRMS (ESI): calcd for $C_{23}H_{21}BrlN_2O_4$ $[M+Na]^+$ 491.0577, found: 491.0573.

tert-butyl (3-(1-cyanovinyl)-1-methyl-2-oxoindolin-3-yl) carbonate(1m)



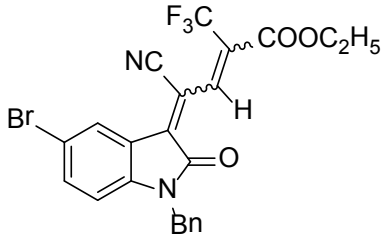
yellow solid. m.p. 113-115℃.^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45-7.37 (m, 2H), 7.16-7.11 (t, *J* = 7.5Hz, 1H), 6.93-6.90 (d, *J*=7.8Hz, 1H), 6.26 (s, 1H), 6.18 (s, 1H), 3.28 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.7, 149.9, 144.2, 133.4, 131.4, 124.6, 123.9, 123.5, 120.2, 115.0, 109.1, 84.4, 79.2, 27.5, 26.8. IR ν_{max} (KBr, film, cm^{-1}): 1758, 1727, 1610, 1471, 1288, 757. HRMS (ESI): calcd for $C_{17}H_{18}N_2O_4$ $[M+Na]^+$ 337.1158, found: 337.1155.

3. General procedureforphosphine-catalyzed Wittig reaction of MBH carbonate with ketone

To a solution of Morita-Baylis-Hillman carbonate**1d** (0.1 mmol) in THF (1 ml)was added PPh_3(1.2 equiv) under Arat room temperature, then 3, 3, 3-trifluoropyruvate**2a** (0.2 mmol, 25μl) was added. The reaction mixture was stirred for 24 h. After concentrated by vacuum, the resulting mixture was purified by column chromatography over silica gel (gradient: petroleum ether / EtOAc = 14: 1) to afford the desired product

Ethyl-4-(1-benzyl-5-bromo-2-oxoindolin-3-ylidene)-4-cyano-2-(trifluoromethyl)-but-2-enoate(3)

red solid.(one isomer). yield 45%.m.p. 141-143℃.^{1}H NMR (300 MHz, CDCl3) δ: 8.37-8.36 (d, *J*=1.5 Hz, 1H), 8.28-8.27 (d, *J*=1.8 Hz, 1H), 7.40-7.37 (dd, *J*=8.4Hz, *J*=2.1Hz, 1H),7.29-7.17 (m, 5H), 6.581-6.56 (d, *J*=8.4Hz, 1H), 4.81 (s, 2H), 4.39-4.32



(q, *J*=7.2Hz), 1.33-1.29 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 164.7, 161.1, 143.9, 137.5, 136.9, 134.2, 131.9 (q, *J*=6.8Hz), 129.9 (q, *J*=32.3Hz), 129.1, 128.4, 128.3, 127.3, 121.4 (q, *J*=272.3Hz), 120.9, 116.3, 113.9, 111.4, 110.4, 62.9, 43.9, 13.9. IR ν_{max} (KBr, film, cm^{-1}): 2217, 1732, 1710, 1602, 1474, 1181, 1138. HRMS (ESI): calcd for $C_{23}H_{16}BrF_3N_2O_3$ [M+Na]$^+$527.0188, found: 527.0189.

red solid(another isomer). yield 24%. m.p. 144-146℃.^{1}H NMR (300 MHz, CDCl3) δ: 8.41 (s, 1H), 8.36-8.35 (d, *J*=1.8 Hz, 1H), 7.50-7.46 (dd, *J*=8.4Hz, *J*=1.8Hz, 1H),7.37-7.25 (m, 5H), 6.67-6.64 (d, *J*=8.4Hz, 1H), 4.90 (s, 2H), 4.43-4.36 (q, *J*=7.2Hz), 1.41-1.37 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 164.4, 161.4, 161.3, 143.9, 144.2, 137.6, 137.5, 137.5, 137.0, 134.2, 129.1, 128.3, 128.2(q, *J*=32.3Hz), 127.3, 121.2(q, *J*=271.5Hz), 120.6, 116.3, 111.5, 108.8, 62.7, 44.0, 14.0. IR ν_{max} (KBr, film, cm^{-1}): 2221, 1726, 1710, 1602, 1470, 1173, 1149. HRMS (ESI): calcd for $C_{23}H_{16}BrF_3N_2O_3$ [M+Na]$^+$ 527.0188, found: 527.0189.

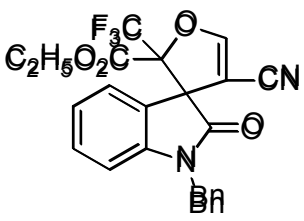
4.General procedure for racemic products of [3+2] annulation of MBH carbonates with ketones

To a solution of Morita-Baylis-Hillman carbonate**1** (0.2 mmol, 78 mg) in EtOAc(1 ml) was added 3, 3, 3-trifluoropyruvate**2** (0.4 mmol, 50 μl) at -40℃. After 5minutes, DABCO (0.04mmol, 5mg) was added. The reaction mixture was stirred for 1-3h till completion as judged by TLC. Then, the mixturewas purified by column chromatographyover silica gel (gradient: petroleum ether / EtOAc = 10~14: 1) to afford the desired racemic product **4**.

5. General procedure for tertiary amine-catalyzed enantioselective [3+2] annulation of MBH carbonates with ketones

To a solution of Morita-Baylis-Hillman carbonate**1**(0.1 mmol, 39 mg) in 1 ml of EtOAc was added 3, 3, 3-trifluoropyruvate**2** (0.2 mmol, 25μl) at -40℃. After 5 minutes, catalyst **5f** (0.02mmol, 9 mg) was added. The reaction mixture was stirred for 1-3h till completion as judged by TLC. Then, the mixtures was purified by column chromatography over silica gel (gradient: petroleum ether / EtOAc = 10~14: 1) to afford the desired product **4**.

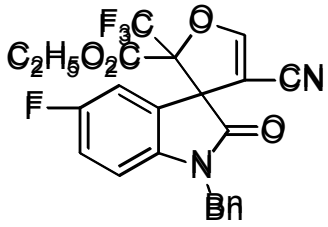
Ethyl1'-benzyl-4-cyano-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4a)



white solid. yield 94%, dr 19:1, ee 97%.$[\alpha]_D^{20}$=+83.7 (*c* 0.92, $CHCl_3$). m.p. 104-106℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.34 (s, 1H), 7.33-7.24 (m, 6H), 7.08-7.01 (m, 2H), 6.03-6.71 (d, *J*=8.1Hz, 1H), 5.31-5.26 (d, *J*=15.9Hz, 1H), 4.74-4.69 (d, *J* = 15.9Hz, 1H), 3.94-3.83 (dq, *J*=10.8Hz, *J*=7.2Hz, 1H),

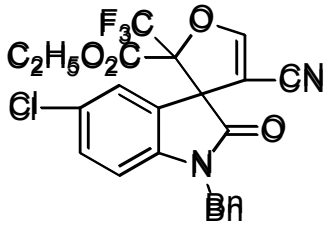
3.67-3.56 (dq, *J*=10.8Hz, *J*=7.2Hz, 1H), 0.72-0.67 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.6, 161.0, 159.6, 142.6, 134.7, 131.4, 131.0, 128.9, 128.0, 127.2, 124.6, 123.4, 121.0 (q, *J*=286.5Hz), 110.8, 109.9, 94.7 (q, *J*=31.5Hz), 93.9, 63.6, 60.7, 44.7, 13.1. IR ν_{max} (KBr, film, cm^{-1}): 2232, 1763, 1734, 1640, 1489, 1148.HRMS (ESI): calcd for $C_{23}H_{17}F_3N_2O_4$ [M+H]$^+$443.1213, found: 443.1213. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 0.8 mL·min^{-1}, t_R = 23.1 min (minor), 36.8 min (major)].

Ethyl 1'-benzyl-4-cyano-5'-fluoro-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4b)



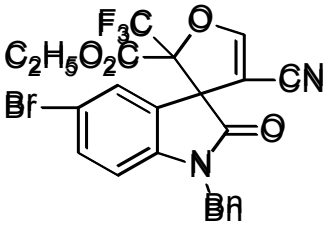
white solid. yield93%, dr 14:1, ee96%. [α]$_D^{20}$ =+72.0 (*c* 0.86, $CHCl_3$). m.p. 132-134 ℃ .^{1}H NMR (300 MHz, CDCl3) δ: 7.61 (s, 1H), 7.37-7.26 (m, 5H), 7.02-6.95 (td,*J*=9.0Hz, *J*=2.7Hz, 1H), 6.86-6.83 (dd, *J*=7.5Hz, *J*=2.7Hz,1H), 6.74-6.63(d,*J*=8.7Hz, *J*=4.2Hz, 1H), 5.27-5.22 (d, *J*=15.6Hz, 1H), 4.75-4.70 (d, *J* = 15.6Hz, 1H), 4.03-3.92 (dq, *J*=10.5Hz, *J*=6.9Hz,1H), 3.83-3.71 (dq, *J*=10.5Hz, *J*=6.9Hz,1H), 0.83-0.78 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.3, 160.7, 159.8, 159.2 (d, *J*=255.8Hz), 138.6 (d, *J*=2.3Hz), 134.3, 129.0, 128.1, 127.1, 126.0 (d, *J*=7.5Hz), 120.9 (q, *J*=286.5Hz), 117.9 (d, *J*=23.5Hz), 112.9 (d, *J*=26.3Hz), 110.8 (d, *J*=7.5Hz), 110.5, 94.3 (q, *J*=31.5Hz), 93.5, 63.8, 60.9, 44.9, 13.18. IR ν_{max} (KBr, film, cm^{-1}): 2231, 1762, 1732, 1635, 1493, 1149.HRMS (ESI): calcd for $C_{23}H_{16}F_4N_2O_4$ [M+H]$^+$ 461.1120, found: 461.1119. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 14.5 min (minor), 26.5 min (major)].

Ethyl 1'-benzyl-5'-chloro-4-cyano-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4c)



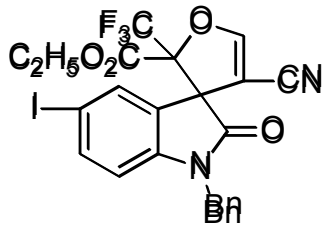
white solid. yield91%,dr 12:1,ee93%.[α]$_D^{20}$=+76.5 (*c* 1.00, $CHCl_3$). m.p. 163-165℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.62 (s, 1H), 7.34-7.23 (m, 6H), 7.07-7.06 (d, *J*=1.5Hz, 1H), 6.66-6.63 (d, *J*=8.4Hz, 1H), 5.26-5.21 (d, *J*=15.9Hz, 1H), 4.77-4.71 (d, *J* = 15.9Hz, 1H), 4.04-3.93 (dq, *J*=10.8Hz, *J*=7.2Hz, 1H), 3.85-3.74 (dq, *J*=10.8Hz, *J*=7.2Hz, 1H), 0.86-0.81 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.1, 160.9, 159.8, 141.1, 134.1, 131.3, 129.0, 128.9, 128.2, 127.1, 126.2, 125.0, 121.0 (q, *J*=286.5Hz), 111.0, 110.5, 94.3 (q, *J*=33.0Hz), 93.5, 63.9, 60.9, 44.9, 13.2. IR ν_{max} (KBr, film, cm^{-1}): 2230, 1763, 1734, 1635, 1483, 1175. HRMS (ESI): calcd for$C_{23}H_{16}ClF_3N_2O_4$ [M+H]$^+$ 477.0823, found: 477.0824.HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 15.4 min (minor), 36.4 min (major)].

Ethyl 1'-benzyl-5'-bromo-4-cyano-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4d)



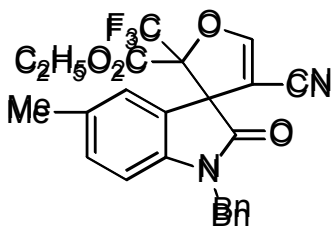
white solid. yield86%, dr 17:1, ee95%.$[\alpha]_D^{20}$=+64.4 (*c* 0.9, $CHCl_3$). m.p. 184-186℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.62 (s, 1H), 7.41-7.26 (m, 6H), 7.20-7.19 (d, *J*=1.8Hz, 1H), 6.61-6.58 (d, *J*=8.4Hz, 1H), 5.25-5.20 (d, *J*=15.9Hz, 1H), 4.77-4.71 (d, *J* = 15.9Hz, 1H), 4.04-3.93 (dq, *J*=10.5Hz, *J*=7.2Hz, 1H), 3.86-3.75 (dq, *J*=10.5Hz, *J*=7.2Hz, 1H), 0.87-0.82 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.1, 160.9, 159.9, 141.6, 134.2, 134.1, 129.0, 128.2, 127.7, 127.1, 126.5, 120.9 (q, *J*=286.5Hz), 115.9, 111.5, 110.5, 94.3, (q, *J*=31.5Hz), 93.5, 63.9, 60.6, 44.9, 13.3. IR ν_{max} (KBr, film, cm^{-1}): 2230, 1764, 1735, 1635, 1481, 1158. HRMS (ESI): calcd for $C_{23}H_{16}BrF_3N_2O_4$ $[M+H]^+$ 521.0319, found: 521.0318. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 15.6 min (minor), 24.0 min (major)].

Ethyl 1'-benzyl-4-cyano-5'-iodo-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4e)



white solid. yield95%,dr >20:1,ee 97%.$[\alpha]_D^{20}$=+43.8 (*c* 1.20, $CHCl_3$). m.p. 183-185 ℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.61 (s, 1H), 7.60-7.56 (dd, *J*=8.1Hz, *J*=1.5Hz, 1H), 7.37-7.28 (m, 6H), 6.50-6.47(d,*J*=8.4Hz,1H), 5.23-5.18 (d, *J*=15.9Hz, 1H), 4.76-4.71 (d, *J* = 15.9Hz, 1H), 4.04-3.93 (dq, *J*=10.8Hz, *J*=7.2Hz,1H), 3.86-3.76 (dq, *J*=10.8Hz, *J*=7.2Hz,1H), 0.89-0.84 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 167.8, 160.0, 158.8, 141.3, 139.1, 133.0, 132.2, 128.0, 127.1, 126.0, 125.7, 119.8 (q, *J*=285.8Hz), 110.9, 109.5, 93.3 (q, *J*=32.3Hz), 92.5, 84.2, 62.9, 59.4, 43.8, 12.31. IR ν_{max} (KBr, film, cm^{-1}): 2231, 1767, 1743, 1634, 1480, 1158. HRMS (ESI): calcd for $C_{23}H_{16}F_3IN_2O_4$ $[M+H]^+$ 569.0179, found: 569.0179. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 18.8 min (minor), 23.8 min (major)].

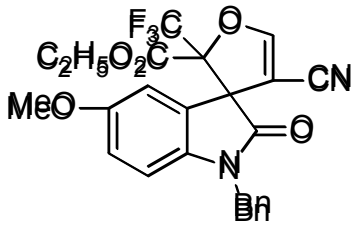
Ethyl 1'-benzyl-4-cyano-5'-methyl-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4f)



white solid. yield85%,dr 17:1,ee94%.$[\alpha]_D^{20}$=+71.8 (*c* 0.78, $CHCl_3$). m.p. 164-166 ℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.52 (s, 1H), 7.26-7.18 (m, 5H), 6.99-6.96 (d, *J*=7.8Hz, 1H), 6.80 (s, 1H), 6.53-6.50 (d, *J*=8.1Hz, 1H), 5.19-5.14 (d, *J*=15.6Hz, 1H), 4.66-4.60 (d, *J* = 15.6Hz, 1H), 3.87-3.76 (dq, *J*=10.8Hz, *J*=7.2Hz, 1H), 3.62-3.52 (dq, *J*=10.8Hz, *J*=7.2Hz, 1H), 0.66-0.62 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.5, 161.1, 159.3, 140.2, 134.8, 133.2, 131.6, 128.9, 127.9, 127.1, 125.3, 124.6, 121.0 (q, *J*=286.5Hz), 110.9, 109.7, 94.4 (q, *J*=31.5Hz), 93.8, 63.5, 60.7, 44.7, 20.9, 13.1. IR ν_{max} (KBr, film, cm^{-1}): 2230, 1764, 1730, 1637, 1499, 1153.HRMS (ESI): calcd for $C_{24}H_{19}F_3N_2O_4$ $[M+H]^+$ 457.1371, found: 457.1370. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 14.0 min

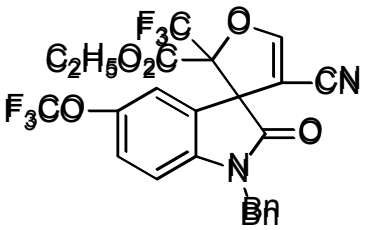
(minor), 21.9 min (major)].

Ethyl 1'-benzyl-4-cyano-5'-methoxy-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4g)



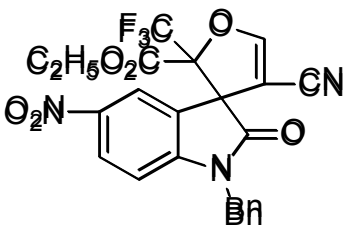
white solid. yield81%,dr 14:1,ee 97%.$[\alpha]_D^{20}$=+68.4 (*c* 0.76, $CHCl_3$). m.p. 158-160℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.60 (s, 1H), 7.32-7.27 (t, 5H), 6.80-6.76 (dd, *J*=8.7Hz, *J*=2.4Hz 1H), 6.67-6.66 (d, *J*=2.1Hz, 1H), 6.62-6.59 (d, *J*=8.7Hz, 1H),5.27-5.22 (d, *J*=15.9Hz, 1H), 4.72-4.67 (d, *J* = 15.9Hz, 1H), 3.96-3.88 (dq, *J*=10.8Hz, *J*=7.2Hz, 1H), 3.72-3.66 (m, 4H), 0.77-0.73 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.2, 161.1, 159.4, 156.4, 135.8, 134.7, 128.9, 128.0, 127.1, 125.6, 121.0(q, *J*=286.5Hz), 116.0, 111.6,110.8, 110.5, 94.4 (q, *J*=31.5Hz), 94.1, 63.6, 60.0, 55.9, 44.8, 13.1. IR ν_{max} (KBr, film, cm^{-1}): 2228, 1764, 1731, 1626, 1497, 1165.HRMS (ESI): calcd for $C_{24}H_{19}F_3N_2O_5$ $[M+H]^+$473.1321, found: 473.1319. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.3 mL·min^{-1}, t_R = 16.9 min (minor), 52.3 min (major)].

Ethyl 1'-benzyl-4-cyano-2'-oxo-5'-(trifluoromethoxy)-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4h)



white solid. yield89%, dr 9:1, ee96%.$[\alpha]_D^{20}$=+85.7 (*c* 0.56, $CHCl_3$). m.p. 112-114℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.63 (s, 1H), 7.38-7.28 (m, 5H), 7.17-7.15 (d, *J* = 8.4Hz, 1H), 7.00 (s, 1H),6.74-6.71 (d, *J*=8.7Hz, 1H), 5.32-5.27 (d, *J*=15.9Hz, 1H), 4.75-4.69 (d, *J* = 15.9Hz, 1H), 4.00-3.89 (dq, *J*=10.5Hz, *J*=6.9Hz, 1H), 3.78-3.67 (dq, *J*=10.5Hz, *J*=6.9Hz, 1H), 0.81-0.76 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.3, 161.1, 159.9, 144.9, 144.9, 141.3, 134.0, 129.1, 128.2, 127.1, 126.0, 125.5, 125.1, 124.6, 122.7, 122.1, 120.7(q, *J*=286.5Hz), 120.3(q, *J*=256.5Hz), 118.7, 94.4 (q, *J*=31.5Hz), 93.4, 63.7, 60.6, 44.9, 13.1. IR ν_{max} (KBr, film, cm^{-1}): 2231, 1764, 1745, 1635, 1498, 1152. HRMS (ESI): calcd for $C_{24}H_{16}F_6N_2O_5$ $[M+H]^+$527.1039, found: 527.1036. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 10.0 min (minor), 11.8 min (major)].

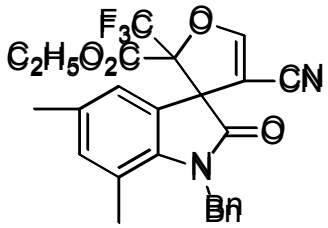
Ethyl 1'-benzyl-4-cyano-5'-nitro-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4i)



white solid. yield90%, dr 17:1, ee96%.$[\alpha]_D^{20}$=+83.6 (*c* 0.86, $CHCl_3$). m.p. 132-134℃.^{1}H NMR (300 MHz, CDCl3) δ: 8.26-8.22 (dd, *J*=9.0Hz, *J*=2.4Hz,1H),8.00-7.99(d,*J*=2.1Hz,1H), 7.70 (s, 1H), 7.39-7.30 (m, 5H), 6.86-6.84 (d,*J*=8.7Hz,1H), 5.30-5.24 (d, *J*=15.9Hz, 1H), 4.88-4.23 (d, *J* = 15.9Hz, 1H),

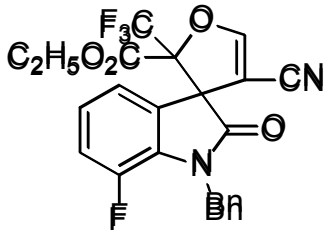
4.03-3.93 (dq, *J*=10.8Hz, *J*=7.2Hz,1H), 3.86-3.75 (dq, *J*=10.8Hz, *J*=7.2Hz,1H), 0.92-0.87 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.6, 160.8, 160.6, 148.0, 143.7, 133.4, 129.2, 128.5, 128.1, 127.1, 125.6, 120.8(q, *J*=286.5Hz), 120.4, 110.2, 109.9, 94.2 (q, *J*=30.0Hz), 92.9, 64.1, 60.4, 45.2 14.3. IR ν_{max} (KBr, film, cm^{-1}): 2229, 1746, 1621, 1605, 1489, 1335, 1151.HRMS (ESI): calcd for $C_{23}H_{16}F_3N_3O_6$ $[M+H]^+$ 488.1064, found: 488.1064. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 35.4 min (minor), 40.8 min (major)].

Ethyl 1'-benzyl-4-cyano-5',7'-dimethyl-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4j)



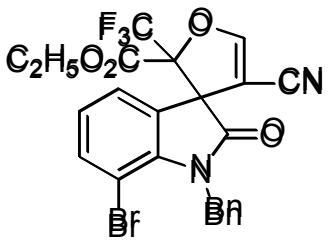
white solid. yield95%,dr>20:1.ee96%.$[\alpha]_D^{20}$=+74.5 (*c* 0.94, $CHCl_3$). m.p. 138-140 ℃ .^{1}H NMR (300 MHz, CDCl3) δ: 7.57 (s, 1H), 7.35-7.21 (m, 5H), 6.85 (s, 1H), 6.74 (s, 1H), 5.41-5.35 (d, *J*=17.1Hz, 1H), 5.12-5.07 (d, *J*=17.1Hz, 1H) 4.74-4.69 (d, *J* = 15.9Hz, 1H), 4.03-3.92 (dq, *J*=10.5Hz, *J*=7.2Hz, 1H), 3.82-3.71 (dq, *J*=10.5Hz, *J*=7.2Hz, 1H), 2.24 (s, 1H), 2.20 (s, 1H), 0.92-0.87 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 170.5, .161.2, 159.1, 138.2, 136.5, 135.7, 133.1, 128.9, 127.4, 125.5, 125.4, 123.2, 121.0(q, *J*=285.7Hz), 120.4, 111.0, 94.6 (q, *J*=30.7Hz), 94.6, 63.6, 60.4, 45.9, 20.6, 18.4, 13.3. IR ν_{max} (KBr, film, cm^{-1}): 2227, 1765, 1743, 1638, 1482, 1162.HRMS (ESI): calcd for $C_{25}H_{21}F_3N_2O_4$ $[M+H]^+$471.1529, found: 471.1526. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 33.7 min (minor), 52.5 min (major)]

Ethyl 1'-benzyl-4-cyano-7'-fluoro-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4k)



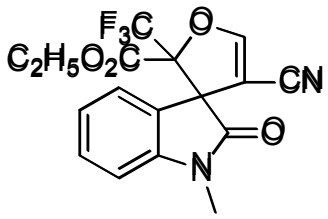
white solid. yield76%,dr >20:1,ee98%.$[\alpha]_D^{20}$=+73.1 (*c* 0.70, $CHCl_3$). m.p. 150-1152 ℃ .^{1}H NMR (300 MHz, CDCl3) δ: 7.59 (s, 1H), 7.37-7.26 (m, 5H), 7.10-6.97 (m, 2H), 6.89-6.86 (dd, *J*=7.2Hz, *J*=1.2Hz, 1H), 5.28-5.23 (d, *J*=15.3Hz, 1H), 4.74-4.69 (d, *J* = 15.3Hz, 1H), 3.95-3.84 (dq, *J*=10.5Hz, *J*=7.2Hz, 1H), 3.72-3.61 (dq, *J*=10.5Hz, *J*=7.2Hz, 1H), 0.72-0.67 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.2, 160.8, 159.6, 147.1 (d, *J*=254.3Hz), 135.8, 129.4 (d, *J*=9.8Hz), 128.7, 127.9, 127.3 (d, *J*=3.3Hz), 127.3, 124.2 (d, *J*=6.0Hz), 120.9(q, *J*=287.3Hz),120.6 (d, *J*=3.8Hz), 119.5 (d, *J*=19.5Hz),110.5, 94.5 (q, *J*=31.5Hz), 93.9, 63.7, 60.7 (d, *J*=2.3Hz), 46.3 (d, *J*=4.5Hz), 13.1. IR ν_{max} (KBr, film, cm^{-1}): 2227, 1769, 1724, 1635, 1488, 1153.HRMS (ESI): calcd for$C_{23}H_{16}F_4N_2O_4$ $[M+H]^+$461.1120, found: 461.1119.HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 14.4 min (minor),25.9 min (major)]

Ethyl-1'-benzyl-7'-bromo-4-cyano-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline]-2-carboxylate(4l)



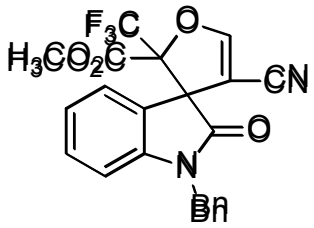
white solid. yield89%, dr>20:1,ee 99%.$[\alpha]_D^{20}$=+72.9 (*c* 0.92, $CHCl_3$). m.p. 137-139℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.61 (s, 1H), 7.48-7.45 (dd, *J*=8.1Hz, *J*=1.2Hz,1H), 7.35-7.23 (m, 5H), 7.05-7.02 (dd, *J*=7.5Hz, *J*=1.2Hz,1H), 6.97-6.92 (t, *J*=7.8Hz, 1H), 5.54-5.49 (d, *J*=16.8Hz, 1H), 5.46-5.41 (d, *J* = 16.8Hz, 1H), 4.03-3.92 (dq, *J*=10.8Hz, *J*=7.2Hz,1H), 3.81-3.70 (dq, *J*=10.8Hz, *J*=7.2Hz,1H), 0.92-0.88 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 170.3, 160.8, 159.6, 140.4, 137.3, 136.2, 128.7, 127.8, 127.4, 126.5, 126.1, 124.5, 123.8, 120.8(q, *J*=287.3Hz), 110.5, 103.0, 94.8 (q, *J*=31.5Hz), 94.8, 63.9, 60.3, 45.6, 13.4. IR ν_{max} (KBr, film, cm^{-1}): 2232, 1774, 1734, 1636, 1464, 1153.HRMS (ESI): calcd for$C_{23}H_{16}BrF_3N_2O_4$ $[M+H]^+$ 521.0324, found: 521.0328. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 15.2 min (minor), 51.5 min (major)].

Ethyl 4-cyano-1'-methyl-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indoline] -2-carboxylate(4m)



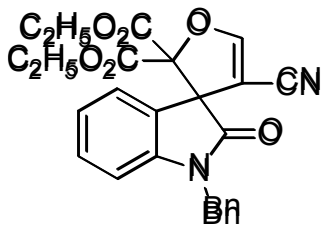
white solid. yield89%,dr 10:1,ee98%.$[\alpha]_D^{20}$=+113.0 (*c* 0.66, $CHCl_3$). m.p. 169-171 ℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.53 (s, 1H), 7.37-7.32 (m, 1H), 7.05-6.98 (m, 2H), 6.83-6.81 (d, *J*=7.8Hz, 1H), 3.93-3.82 (dq, *J*=10.2Hz, *J*=7.2Hz, 1H), 3.68-3.57 (dq, *J*=10.2Hz, *J*=7.2Hz, 1H), 3.22 (s, 1H), 0.81-0.77 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 169.5, 161.1, 159.6, 143.6, 124.6, 124.1, 123.3, 120.9 (q, *J*=285.8Hz), 110.7, 108.8, 94.3 (q, *J*=32.3Hz), 93.6, 63.5, 60.8, 27.3, 13.2. IR ν_{max} (KBr, film, cm^{-1}): 2232, 1761, 1726, 1639, 1472, 1151.HRMS (ESI): calcd for $C_{17}H_{13}F_3N_2O_4$ $[M+H]^+$367.0903, found: 367.0900. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 21.1 min (minor), 22.4 min (major)].

Methyl 1'-benzyl-4-cyano-2'-oxo-2-(trifluoromethyl)-2*H*-spiro[furan-3,3'-indolin -2-carboxylate(4n)



white solid. yield85%, dr 12:1, ee95%.$[\alpha]_D^{20}$=+112.0 (*c* 0.70, $CHCl_3$). m.p. 156-158℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.52 (s, 1H), 7.27-7.15 (m, 6H), 6.98 (s, 1H), 6.96 (s, 1H), 6.64-6.62 (d, *J*=7.8Hz, 1H), 5.18-5.13 (d, *J*=15.9Hz, 1H), 4.74-4.69 (d, *J* = 15.9Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 168.4, 160.6, 158.5, 141.5, 133.5, 130.4, 127.9, 126.9, 126.0, 123.4, 123.4, 122.3, 119.9 (q, *J*=286.5Hz), 109.7, 109.0, 93.6 (q, *J*=31.5Hz), 92.8, 59.8, 52.5, 43.7. IR ν_{max} (KBr, film, cm^{-1}): 2236,1771, 1739, 1636, 1489, 1226, 1155.HRMS (ESI): calcd for $C_{22}H_{15}F_3N_2O_4$ $[M+H]^+$429.1060, found: 429.1057. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.0 mL·min^{-1}, t_R = 19.8 min (minor), 31.8 min (major)]

Diethyl-1'-benzyl-4-cyano-2'-oxo-2*H*-spiro[furan-3,3'-indoline]-2,2-dicarboxylate (4o)

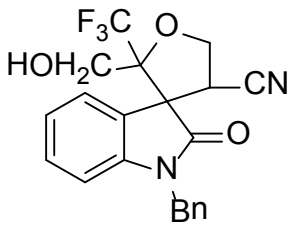


white solid. yield99%, ee94%.$[\alpha]_D^{20}$=+35.6 (*c* 0.90, $CHCl_3$). m.p. 118-120℃.^{1}H NMR (300 MHz, CDCl3) δ: 7.62 (s, 1H), 7.35-7.23 (m, 6H), 7.13-7.10 (d, *J* = 7.2Hz, 1H), 7.06-7.01 (t, *J* = 7.5Hz, 1H), 6.74-6.72 (d, *J*=7.8Hz, 1H), 5.08-5.03 (d, *J*=15.9Hz, 1H), 4.93-4.88 (d, *J* = 15.9Hz, 1H), 4.38-4.19 (m, 1H), 4.14-4.03 (dq, *J*=10.7Hz, *J*=7.2Hz, 1H), 3.97-3.87 (dq, *J*=10.7Hz, *J*=7.2Hz, 1H), 1.28-1.23 (t, *J* = 7.2Hz, 3H), 0.94-0.89 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ: 172.4, 163.4, 163.0, 143.1, 134.7, 130.8, 128.9, 127.8, 127.1, 124.2, 123.4, 111.5, 110.2, 95.3, 93.6, 63.5, 63.1, 62.3, 44.5, 13.8, 13.5. IR ν_{max} (KBr, film, cm^{-1}): 2224, 1751, 1719, 1621, 1469, 1163. HRMS (ESI): calcd for $C_{25}H_{22}N_2O_6$ $[M+H]^+$447.1152, found: 447.1151. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 1.2 mL·min^{-1}, t_R = 40.4 min (minor), 62.6 min (major)].

6. The procedure for the reduction of product 4a

Under N_2 at 0 ℃, to **4a** (0.1mmol) and $LiBH_4$ (0.4 mmol) was added dry THF (2 ml) and dry ethanol (0.1mmol). After 10min, the temperature was allowed to room temperature and the mixture was stirring for overnight. One equivalent of water was added and the mixture was concentrated and extracted with DCM. The organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography over silica gel (gradient: petroleum ether / EtOAc = 6:1) to afford the desired product **5**.

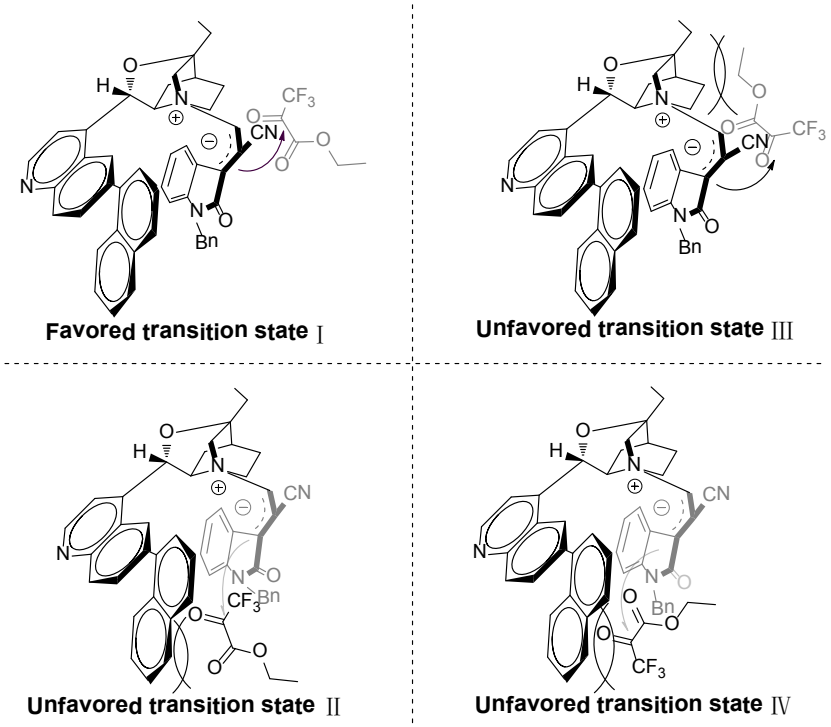
1'-benzyl-2-(hydroxymethyl)-2'-oxo-2-(trifluoromethyl)-4,5-dihydro-2H-spiro[furan-3,3'-indoline]-4-carbonitrile (5)



white solid. yield 45%, 96% ee. $[\alpha]_D^{20}$=+90.6 (*c* 0.27, $CHCl_3$). m.p. 131-132℃.^{1}H NMR (300 MHz, DMSO) δ: 7.82-7.80 (d, *J* = 7.2Hz, 1H), 7.39-7.31 (m, 6H), 7.18-7.13 (t, *J* = 7.3Hz, 1H), 6.97-6.94 (d, *J* = 7.7Hz, 1H), 6.28-6.24 (t, *J*=5.3Hz, 1H), 4.97 (s,2H), 4.79-4.60 (m, 3H), 3.86-3.80 (dd,*J*=11.6Hz, *J*=5.0Hz, 1H), 3.71-3.66 (dd, *J*=11.6Hz, *J*=5.0Hz, 1H), ^{13}C NMR (75 MHz, DMSO) δ: 172.3, 143.4, 135.5, 130.2, 128.5, 127.5, 127.4, 125.9, 123.7(q, *J*=257HZ) 123.1,122.2, 116.7, 109.7, 88.1(q, *J*=88.1Hz), 69.8, 61.9, 59.7, 43.1, 37.8. IR ν_{max} (KBr, film, cm^{-1}): 1710, 1698, 1470, 1337, 1162, 762.HRMS (ESI): calcd for $C_{21}H_{18}N_2O_3F_3$ $[M+H]^+$403.1264, found: 403.1262. HPLC analy1sis [Chiralcel AD, n-hexane/ i-propanol (90:10), 25℃, 0.8 mL·min^{-1}, t_R = 15.6 min (minor), 25.1 min (major)].

7. Plausible catalytic transitional state

The N-allylic ylide intermediate could be stabilized by electron-withdraw cyano group. The *Si*-face of the 1, 3-dipole would be well blocked by quinoline moiety and naphthyl ring of the catalyst, resulting in the approach of trifluoropyruvate to the N-allylic ylide from *Re*-face (**I** and **III**). In addition, because of steric hindrance between quinuclidine cycle of the catalyst and ester group of trifluoropyruvate, transition state **III** is also unfavored. The group at C-6' position played an important role in stereoselective control. Steric hinder 1-naphthyl group at C-6' position may improve the steric hindrance between ester group of trifluoropyruvate and quinuclidine cycle of the catalyst resulting in the increase of diastereoselectivity



Unfavored transition state **II**: Steric hindrance between trifluoropyruvate and the aryl of the catalyst

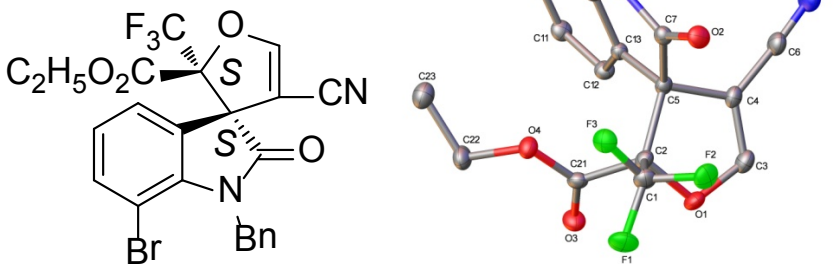
Unfavored transition state **III**: Steric hindrance between ester group of trifluoropyruvate and quinuclidine cycle of the catalyst

Unfavored transition state **IV**: Steric hindrance between trifluoropyruvate and the aryl of the catalyst

8. X-ray crystallography of 4l compound

Crystals of **4l** suitable for X-ray analysis were obtained from ether (CCDC 934201)

The molecular structure of the annulation product **4l** was further confirmed by X-ray crystallographic analysis, which showed that the absolute configurations of two newly created chiral centers were (*S*, *S*).

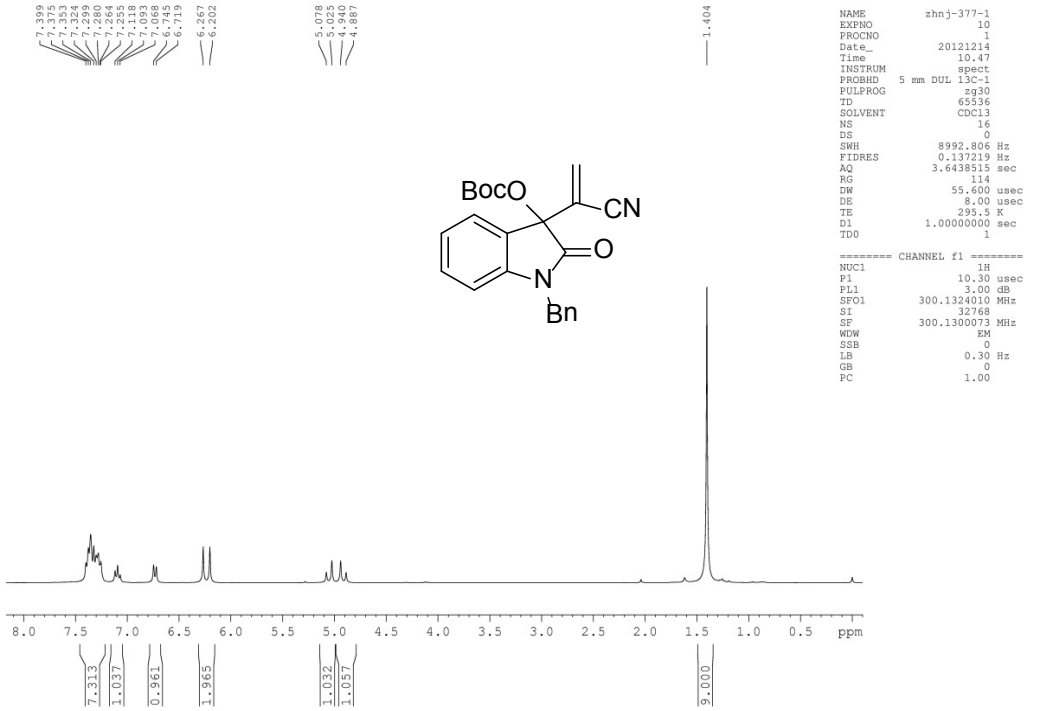


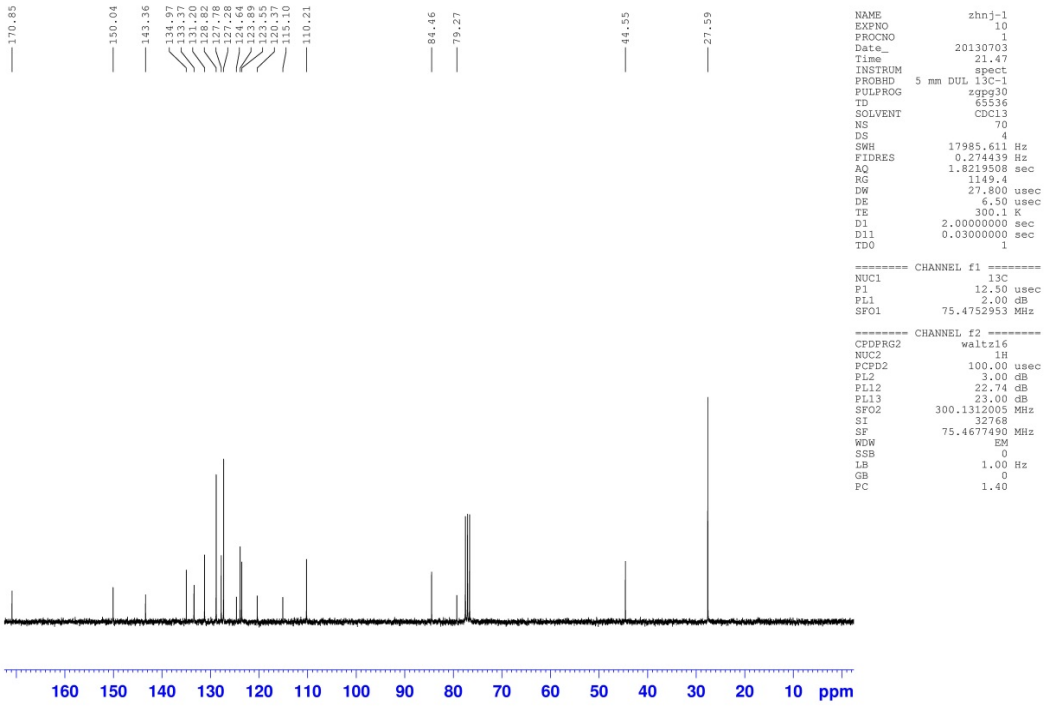
Identification code	**a**
Empirical formula	C23 H16 Br F3 N2 O4
Formula weight	521.29
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 8.0616(16) A alpha = 90 deg.
	b = 10.147(2) A beta = 90 deg.
	c = 26.551(5) A gamma = 90 deg.
Volume	2171.8(7) A^3
Z, Calculated density	4, 1.594 Mg/m^3
Absorption coefficient	1.952 mm^-1
F(000)	1048
Crystal size	0.46 x 0.34 x 0.32 mm
Theta range for data collection	3.05 to 27.47 deg.
Limiting indices	-10<=h<=10, -12<=k<=13, -34<=l<=32
Reflections collected / unique	14343 / 4940 [R(int) = 0.0379]
Completeness to theta = = 27.47	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6779

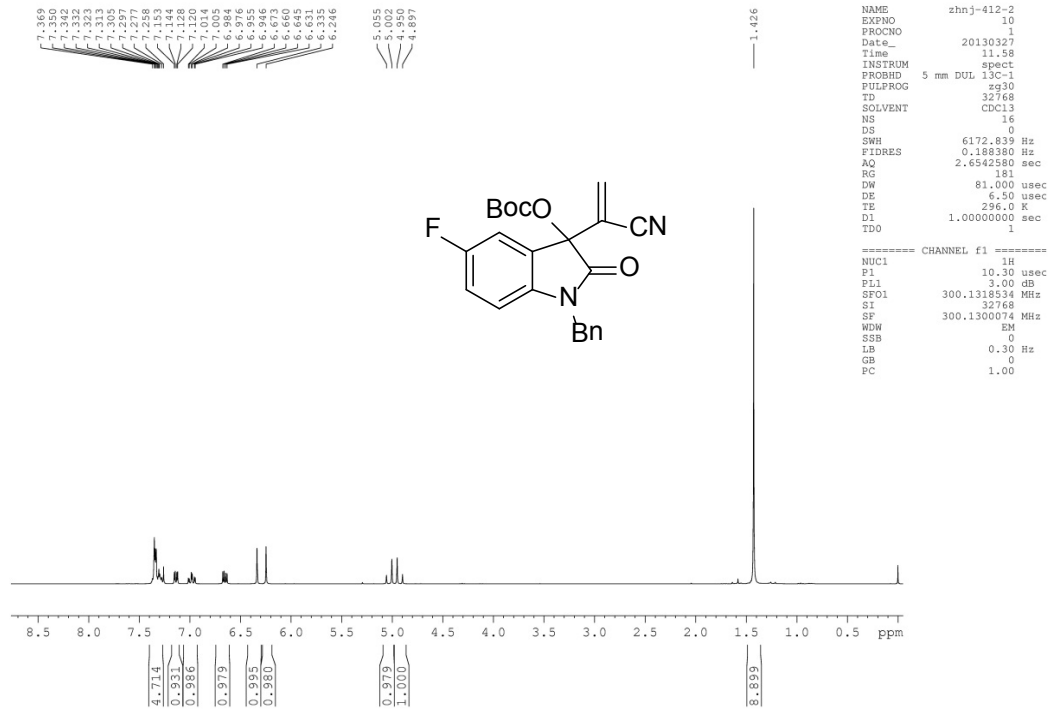
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4940 / 0 / 299
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0741
R indices (all data)	R1 = 0.0383, wR2 = 0.0759
Absolute structure parameter	0.000(7)
Largest diff. peak and hole	0.393 and -0.409 e.A^-3

9. NMR Spectra

9.1NMR Spectra of Substrates





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PROCNO                   1
Date_             20130327
Time                 11.58
INSTRUM              spect
PROBHD    5 mm DUL 13C-1
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      16
DS                       0
SWH              6172.839 Hz
FIDRES           0.188380 Hz
AQ               2.6542580 sec
RG                     181
DW                81.000 usec
DE                 6.50 usec
TE                296.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1          300.1318534 MHz
SI                   32768
SF            300.1300074 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
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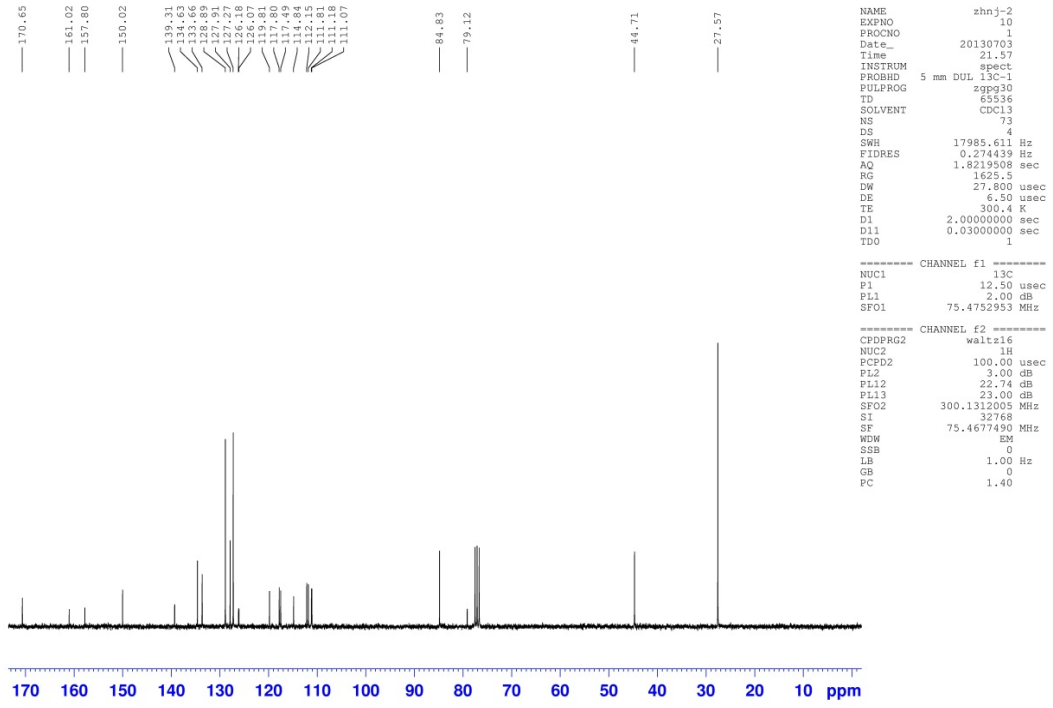


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PROCNO                 1
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INSTRUM            spect
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   73
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                1625.5
DW                27.800 usec
DE                 6.50 usec
TE                300.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2          300.1312005 MHz
SI                   32768
SF            75.4677490 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
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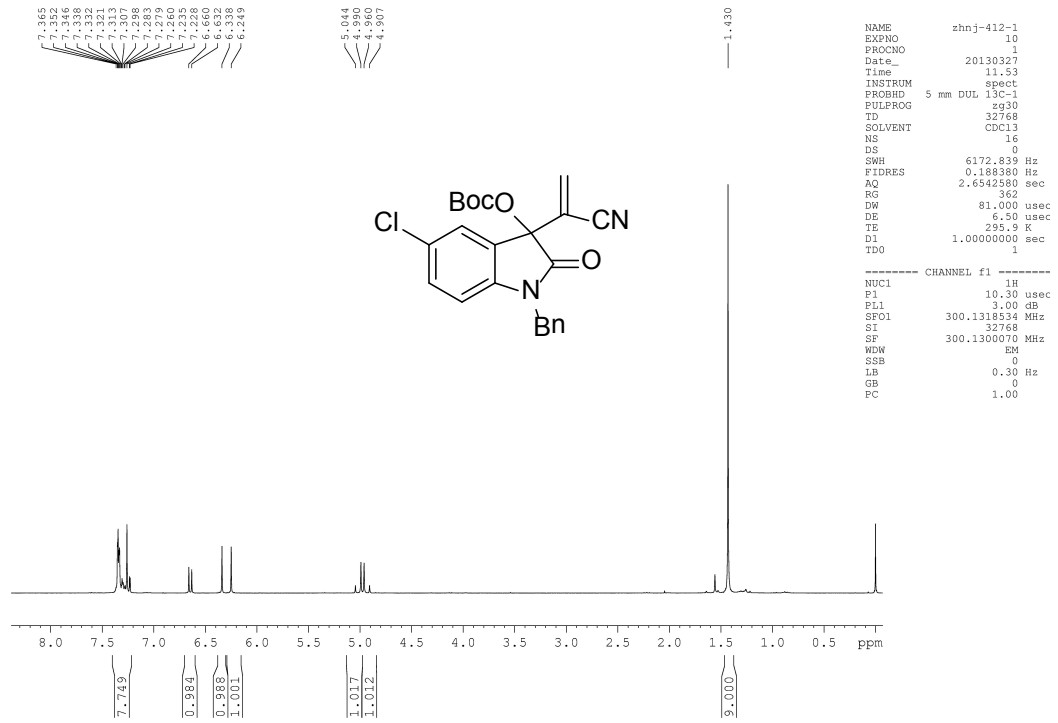


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PROCNO                 1
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Time              11.53
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PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ             2.6542580 sec
RG                  362
DW               81.000 usec
DE                6.50 usec
TE               295.9 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
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SF           300.1300070 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
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PC                 1.00
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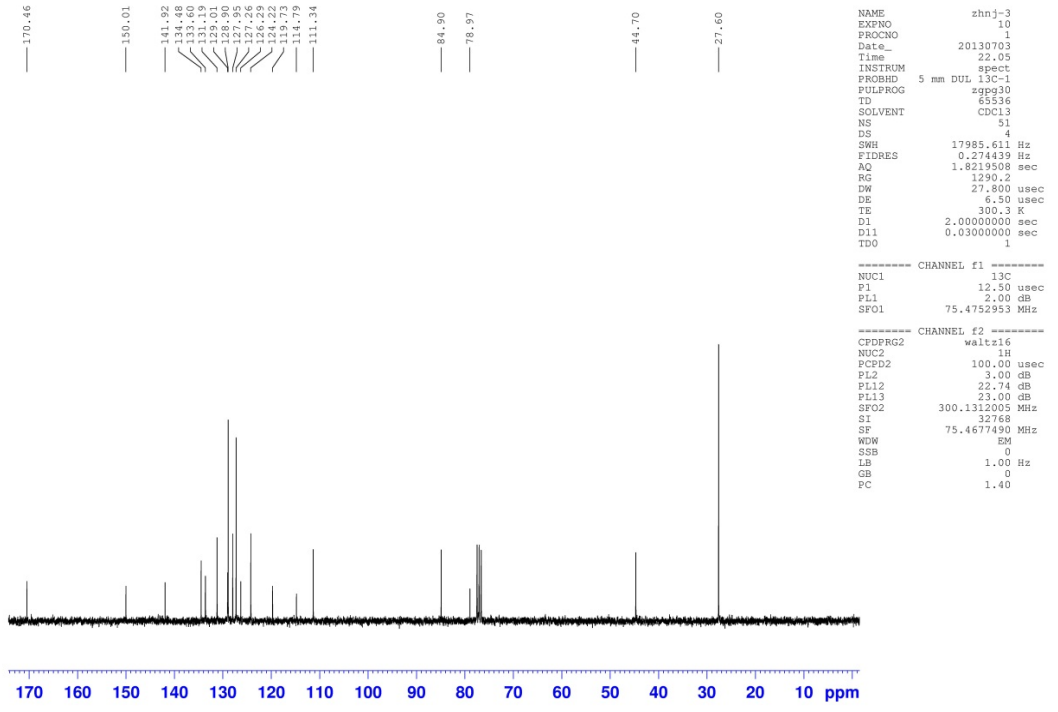


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PROCNO                1
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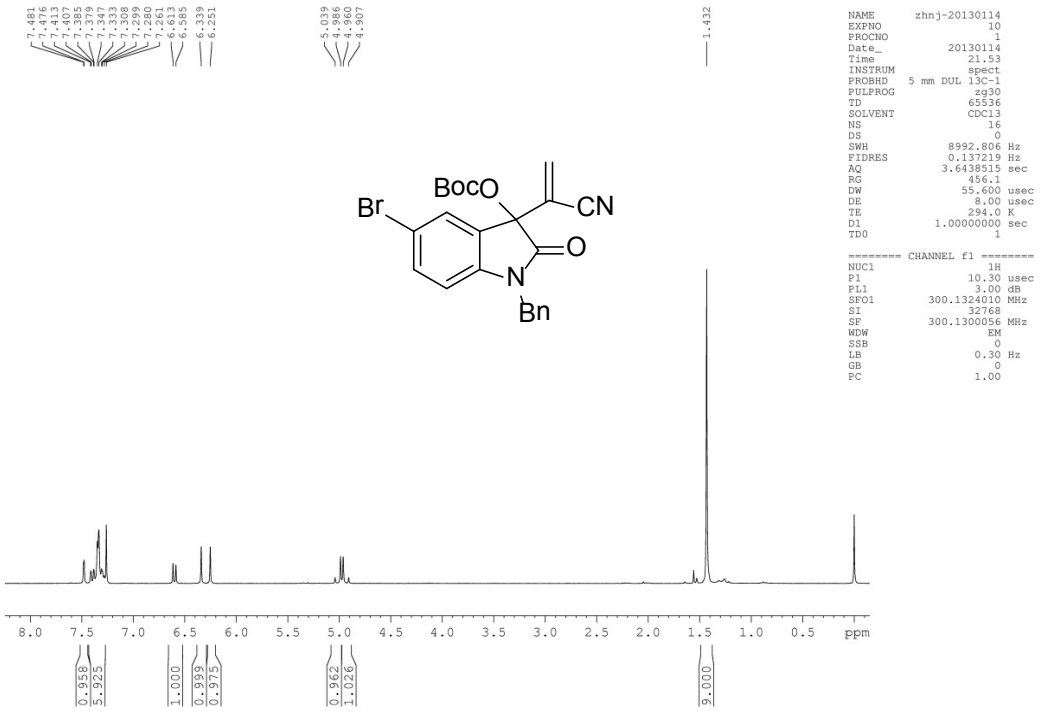
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  51
DS                   4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                1290.2
DW               27.800 usec
DE                6.50 usec
TE               300.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

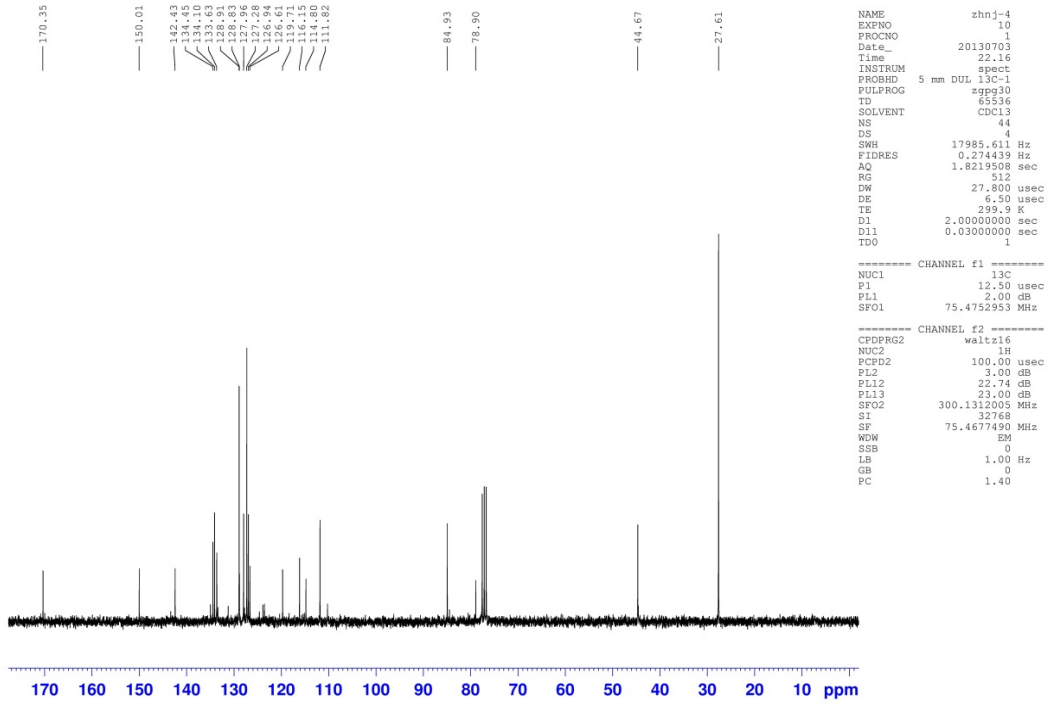
======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                32768
SF           75.4677490 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```




```
NAME                zhnj-20130114
EXPNO                         10
PROCNO                         1
Date_                   20130114
Time                       21.53
INSTRUM                    spect
PROBHD    5 mm DUL 13C-1
PULPROG                     zg30
TD                         65536
SOLVENT                    CDCl3
NS                            16
DS                             0
SWH                     8992.806 Hz
FIDRES                  0.137219 Hz
AQ                      3.6438515 sec
RG                         456.1
DW                        55.600 usec
DE                         8.00 usec
TE                        294.0 K
D1                      1.00000000 sec
TD0                            1

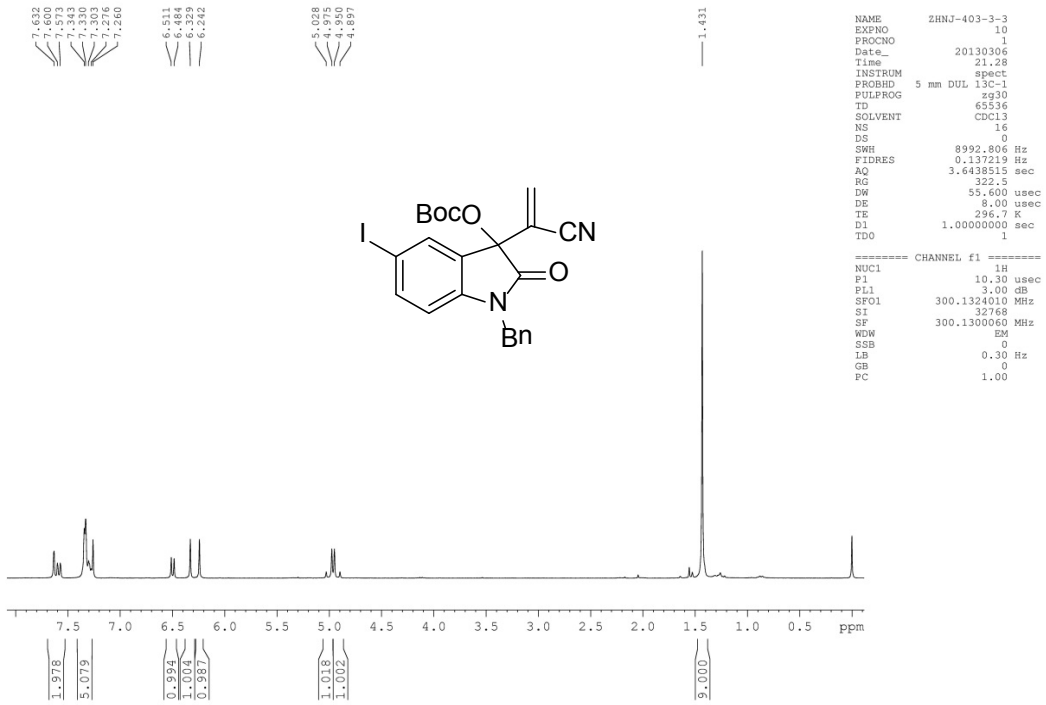
======== CHANNEL f1 ========
NUC1                          1H
P1                         10.30 usec
PL1                         3.00 dB
SFO1                  300.1324010 MHz
SI                         32768
SF                    300.1300056 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```




```
NAME                zhnj-4
EXPNO                   10
PROCNO                   1
Date_             20130703
Time                 22.16
INSTRUM              spect
PROBHD    5 mm DUL 13C-1
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                   44
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                  512
DW                27.800 usec
DE                 6.50 usec
TE                299.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

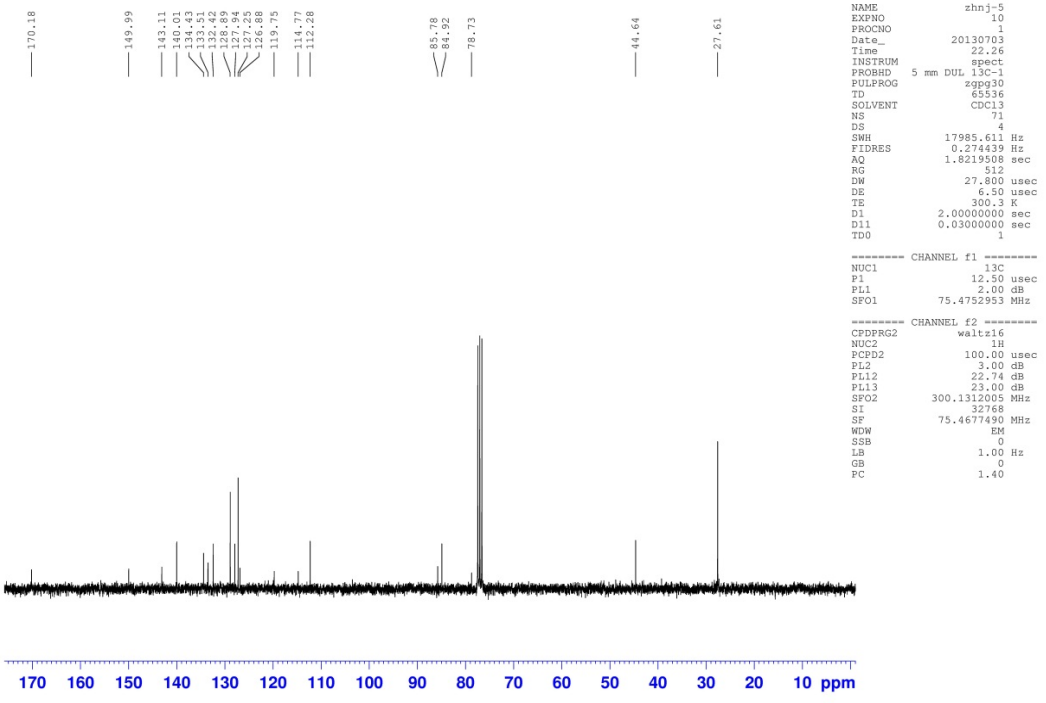
======== CHANNEL f1 ========
NUC1                  13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2          300.1312005 MHz
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```




```
NAME          ZHNJ-403-3-3
EXPNO                   10
PROCNO                   1
Date_             20130306
Time                 21.28
INSTRUM              spect
PROBHD    5 mm DUL 13C-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      16
DS                       0
SWH              8992.806 Hz
FIDRES           0.137219 Hz
AQ               3.6438515 sec
RG                   322.5
DW                  55.600 usec
DE                   8.00 usec
TE                  296.7 K
D1               1.00000000 sec
TD0                      1

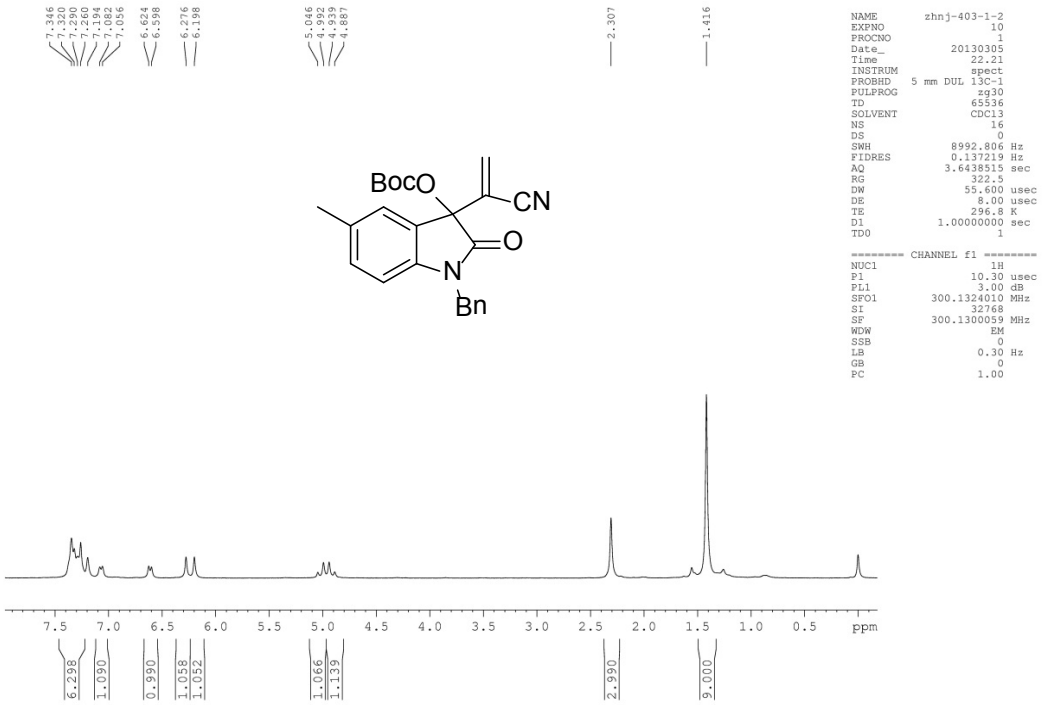
======== CHANNEL f1 ========
NUC1                    1H
P1                   10.30 usec
PL1                   3.00 dB
SFO1           300.1324010 MHz
SI                   32768
SF             300.1300060 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

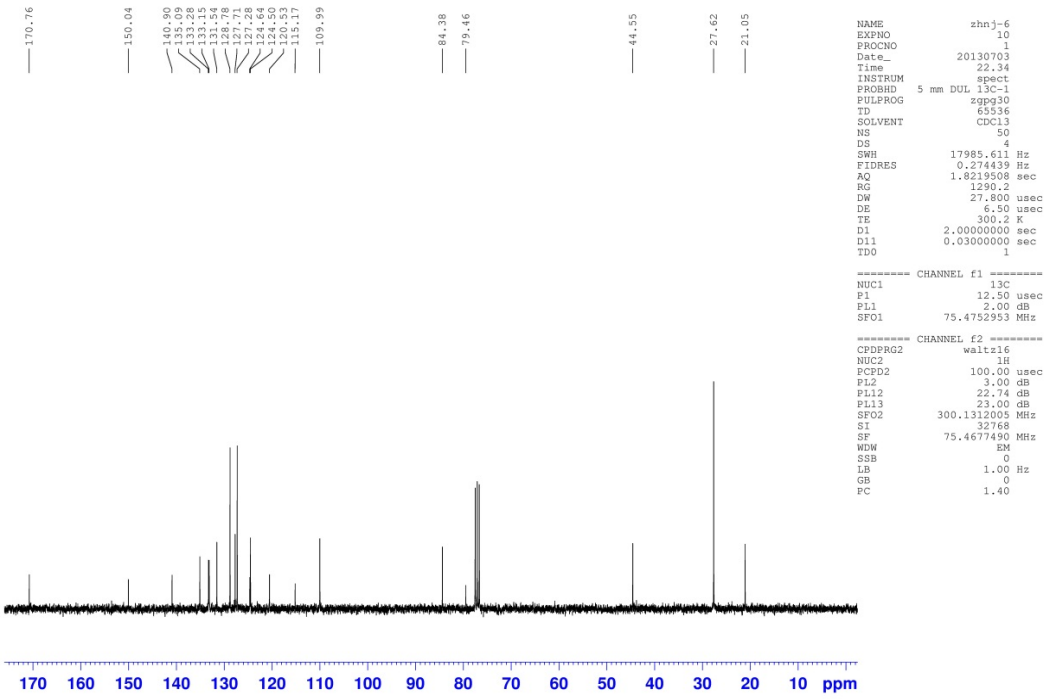


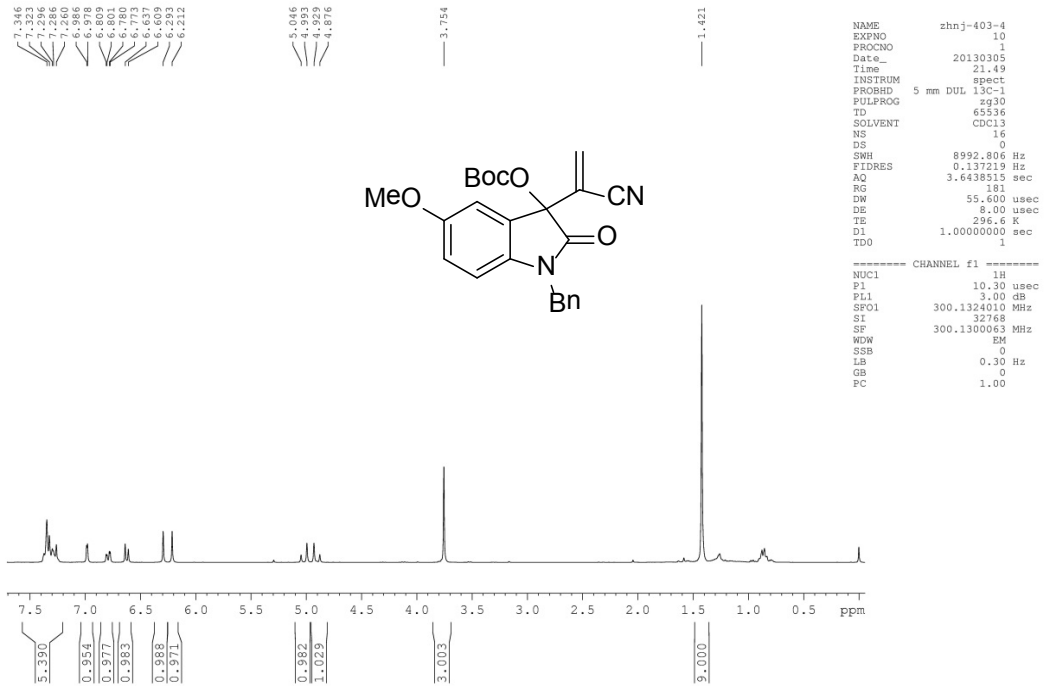

```
NAME                zhnj-5
EXPNO                   10
PROCNO                   1
Date_             20130703
Time                 22.26
INSTRUM              spect
PROBHD    5 mm DUL 13C-1
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                      71
DS                       4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                   512
DW                  27.800 usec
DE                   6.50 usec
TE                  300.3 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   12.50 usec
PL1                   2.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   3.00 dB
PL12                 22.74 dB
PL13                 23.00 dB
SFO2           300.1312005 MHz
SI                   32768
SF             75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

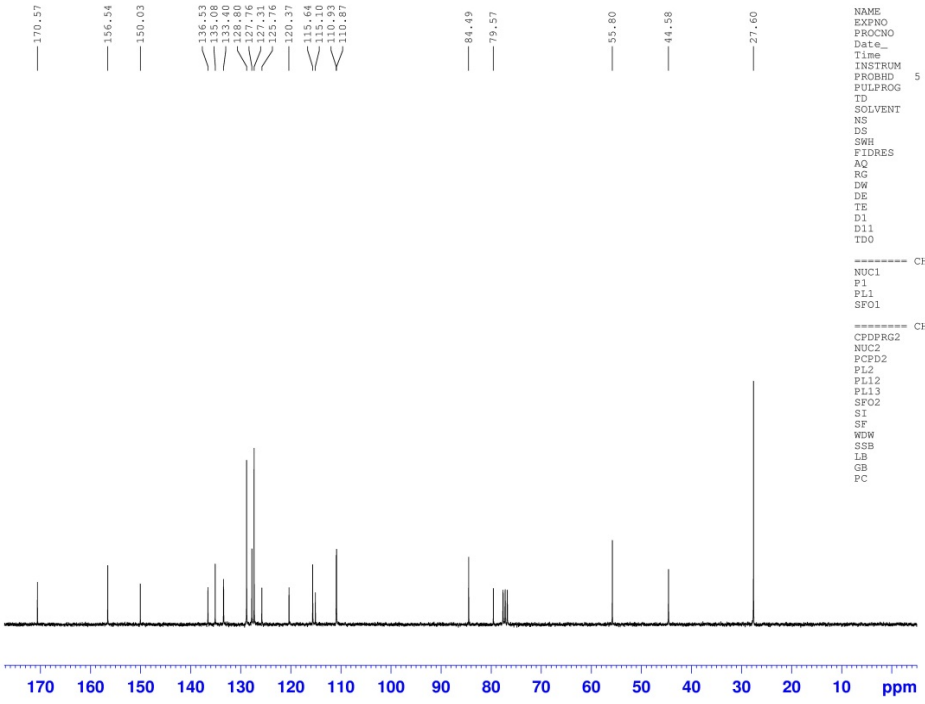

7.346
7.320
7.290
7.260
7.194
7.082
7.056
6.624
6.598
6.276
6.198
5.046
4.992
4.939
4.887
2.307
1.416
BocO
CN
O
N
Bn
NAME zhnj-403-1-2
EXPNO 10
PROCNO 1
Date_ 20130305
Time 22.21
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 322.5
DW 55.600 usec
DE 8.00 usec
TE 296.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1324010 MHz
SI 32768
SF 300.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
6.298
1.090
0.990
1.058
1.052
1.066
1.139
2.990
9.000


170.76
150.04
140.90
135.09
133.28
133.15
131.54
128.78
127.71
127.28
124.64
124.50
120.53
115.17
109.99
84.38
79.46
44.55
27.62
21.05
NAME zhnj-6
EXPNO 10
PROCNO 1
Date_ 20130703
Time 22.34
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 50
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 1290.2
DW 27.800 usec
DE 6.50 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm




```
NAME          zhnj-403-4
EXPNO                 10
PROCNO                 1
Date_           20130305
Time               21.49
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    16
DS                     0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ             3.6438515 sec
RG                   181
DW              55.600 usec
DE               8.00 usec
TE              296.6 K
D1             1.00000000 sec
TD0                    1

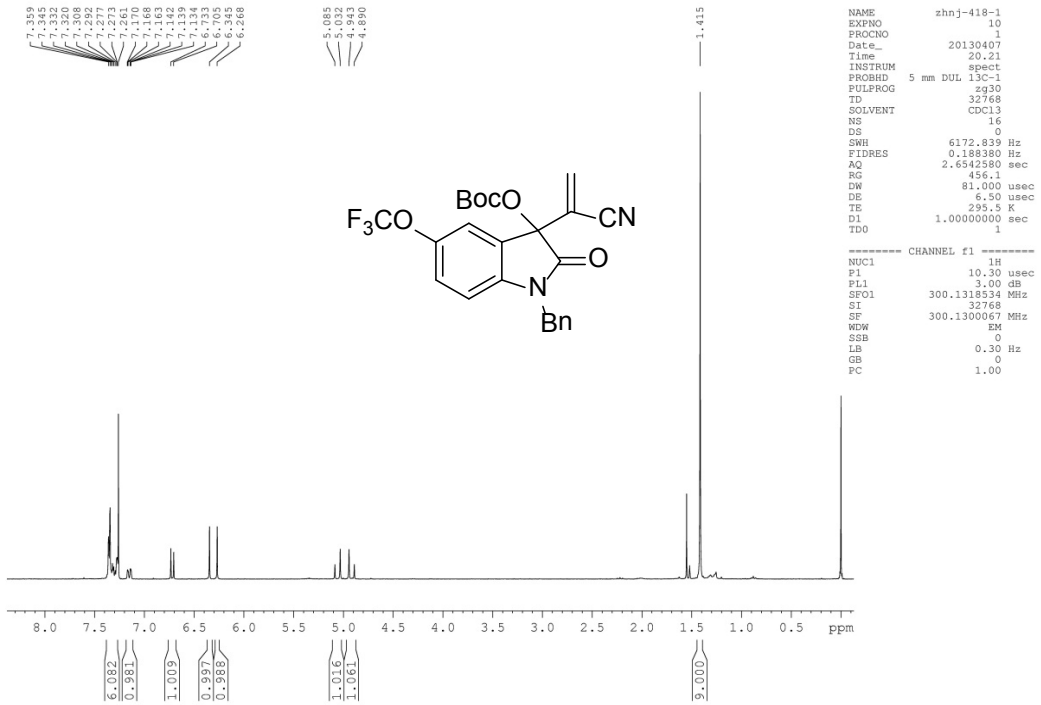
======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1          300.1324010 MHz
SI                 32768
SF            300.1300063 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```




```
NAME             zhnj-7
EXPNO                10
PROCNO                1
Date_          20130704
Time              10.13
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   61
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                 2048
DW              27.800 usec
DE               6.50 usec
TE              300.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1

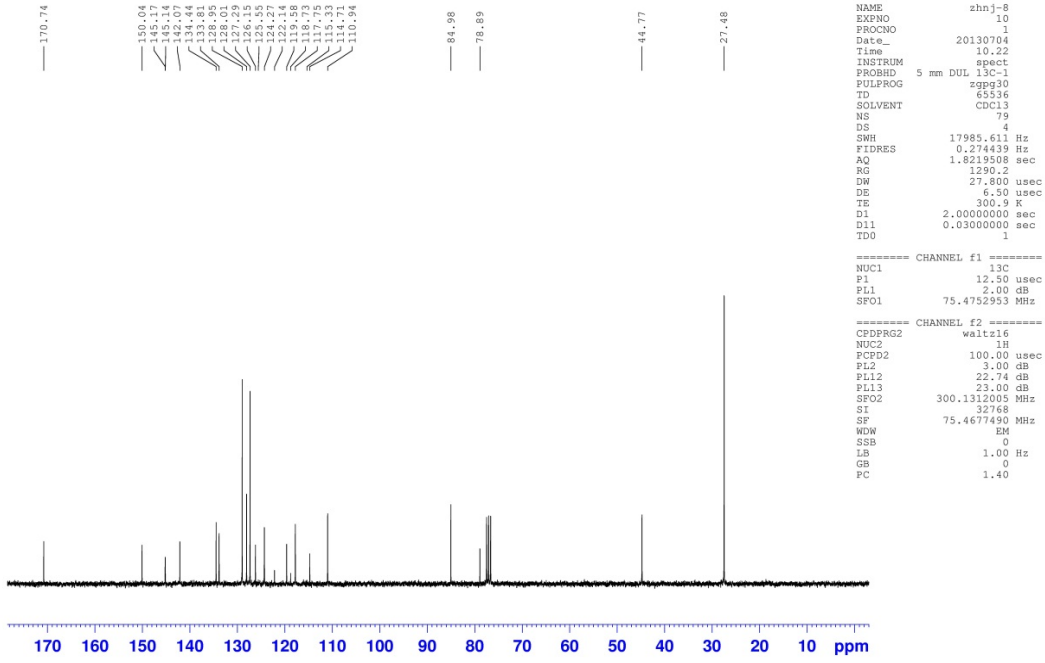
======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2          300.1312005 MHz
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```




```
NAME            zhnj-418-1
EXPNO                   10
PROCNO                   1
Date_             20130407
Time                 20.21
INSTRUM              spect
PROBHD    5 mm DUL 13C-1
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               6172.839 Hz
FIDRES               0.188380 Hz
AQ                2.6542580 sec
RG                   456.1
DW                  81.000 usec
DE                   6.50 usec
TE                  295.5 K
D1                1.00000000 sec
TD0                      1

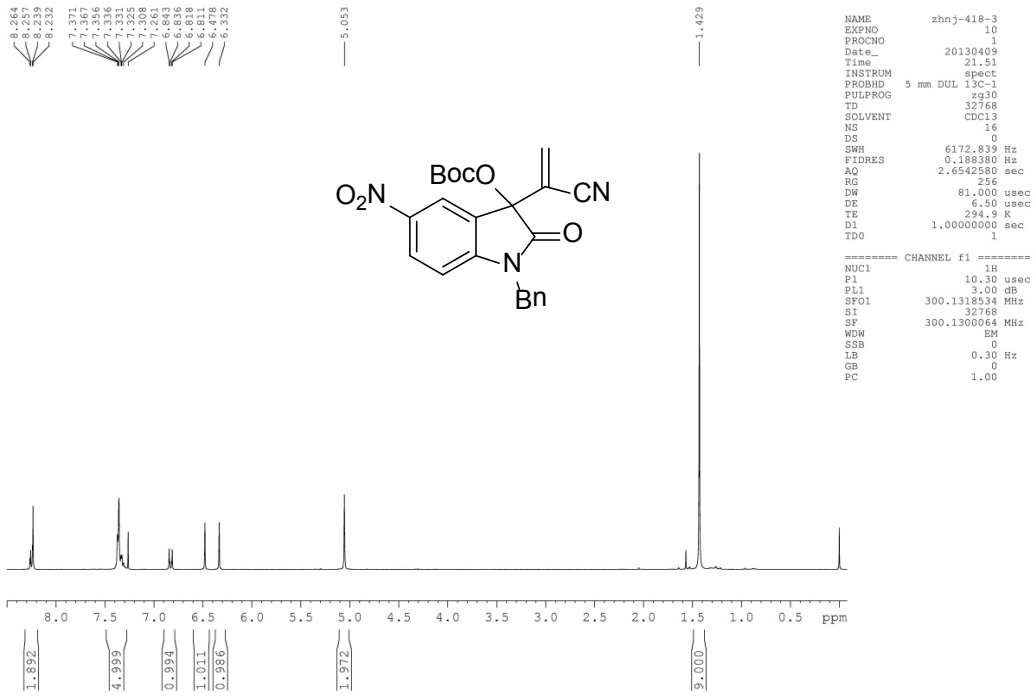
======== CHANNEL f1 ========
NUC1                    1H
P1                   10.30 usec
PL1                   3.00 dB
SFO1           300.1318534 MHz
SI                   32768
SF             300.1300067 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

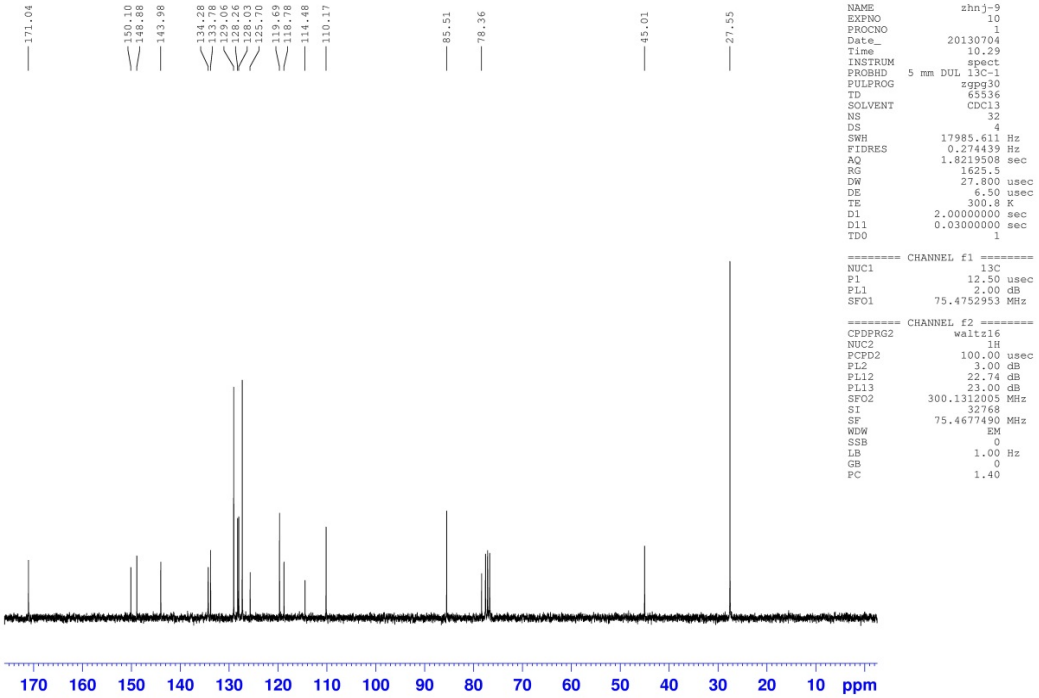


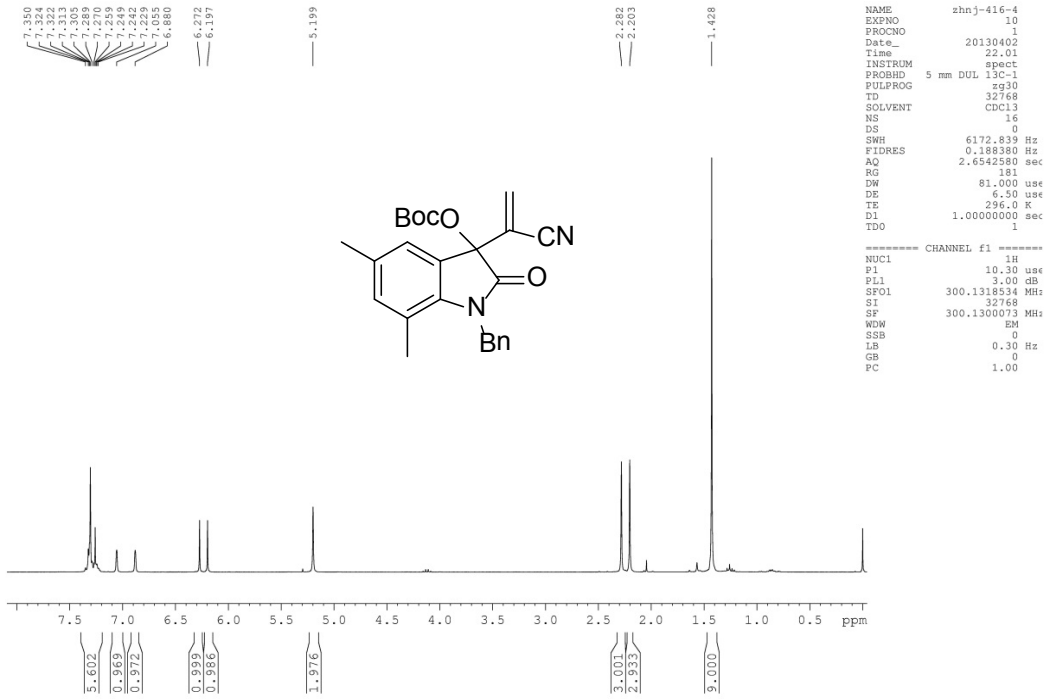

```
NAME                zhnj-8
EXPNO                   10
PROCNO                   1
Date_             20130704
Time                 10.22
INSTRUM              spect
PROBHD    5 mm DUL 13C-1
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      79
DS                       4
SWH              17985.611 Hz
FIDRES               0.274439 Hz
AQ                1.8219508 sec
RG                  1290.2
DW                  27.800 usec
DE                   6.50 usec
TE                  300.9 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                      1

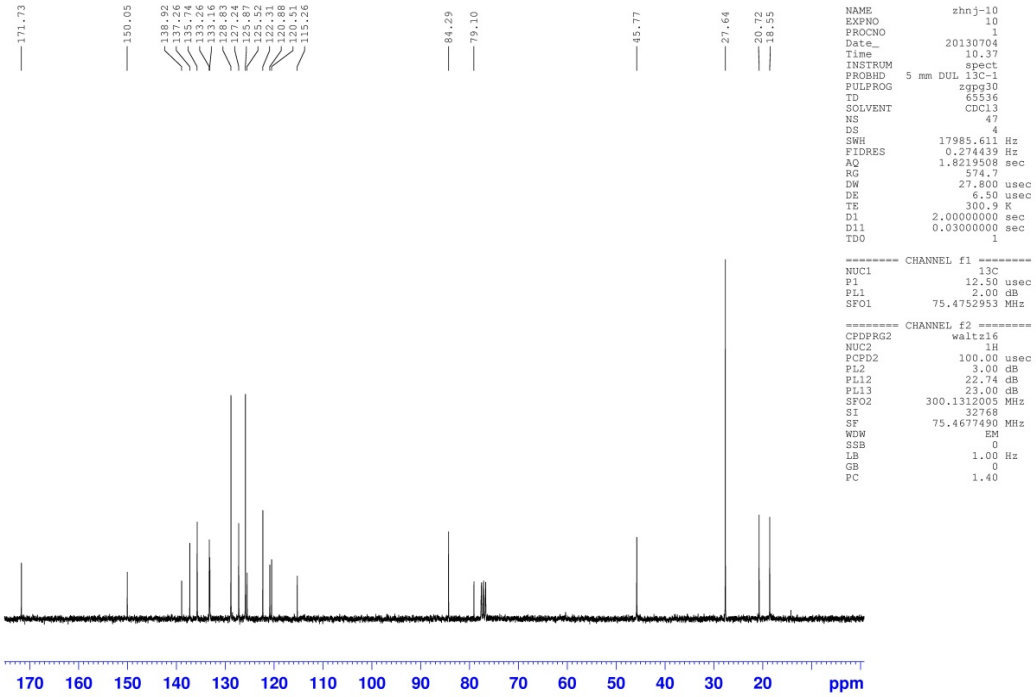
======== CHANNEL f1 ========
NUC1                    13C
P1                   12.50 usec
PL1                   2.00 dB
SFO1           75.4752953 MHz

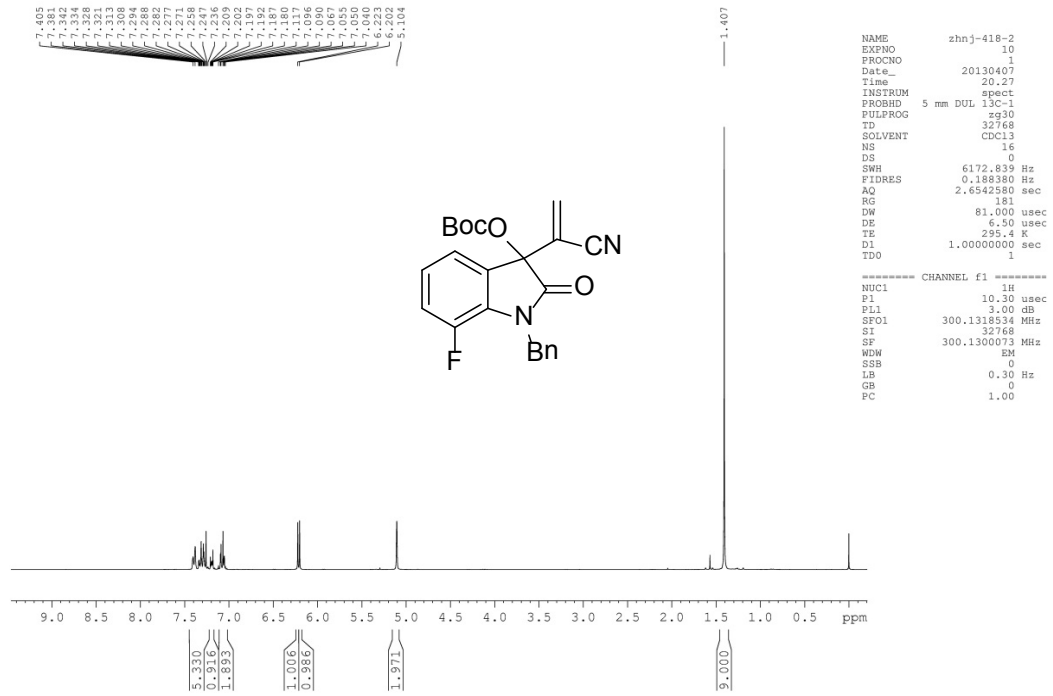
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   3.00 dB
PL12                 22.74 dB
PL13                 23.00 dB
SFO2           300.1312005 MHz
SI                   32768
SF             75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

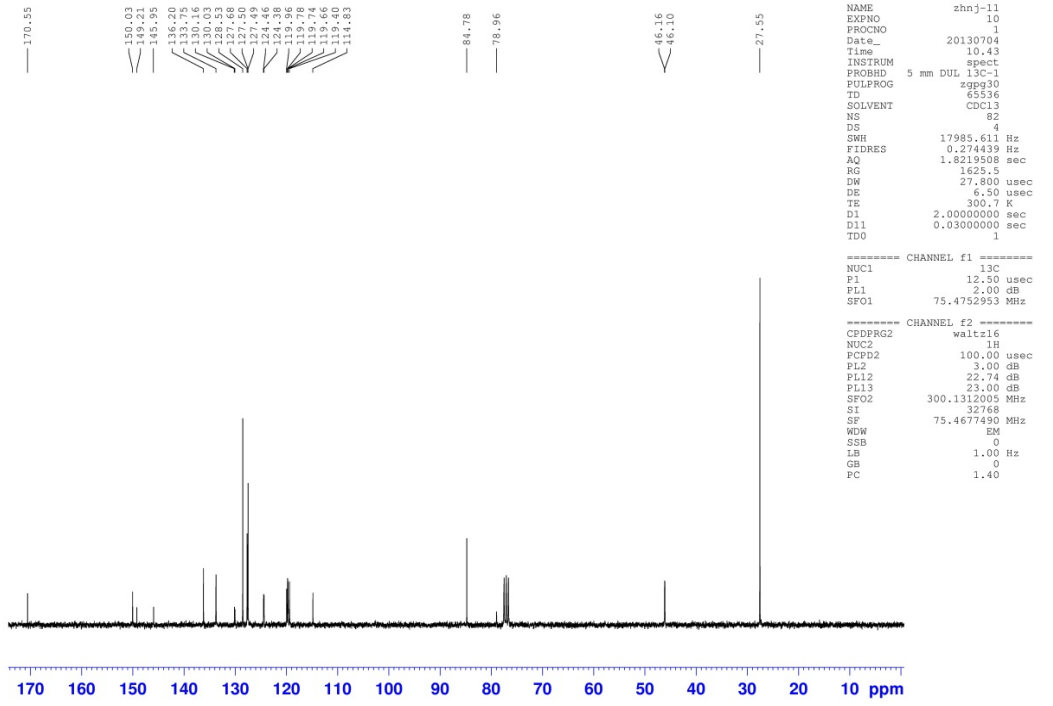

8.264
8.257
8.239
8.232
7.371
7.367
7.356
7.336
7.331
7.325
7.308
7.261
6.843
6.836
6.818
6.811
6.478
6.332
5.053
1.429
BocO
CN
O2N
O
N
Bn
NAME zhnj-418-3
EXPNO 10
PROCNO 1
Date_ 20130409
Time 21.51
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 256
DW 81.000 usec
DE 6.50 usec
TE 294.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.892
4.999
0.994
1.011
0.986
1.972
9.000

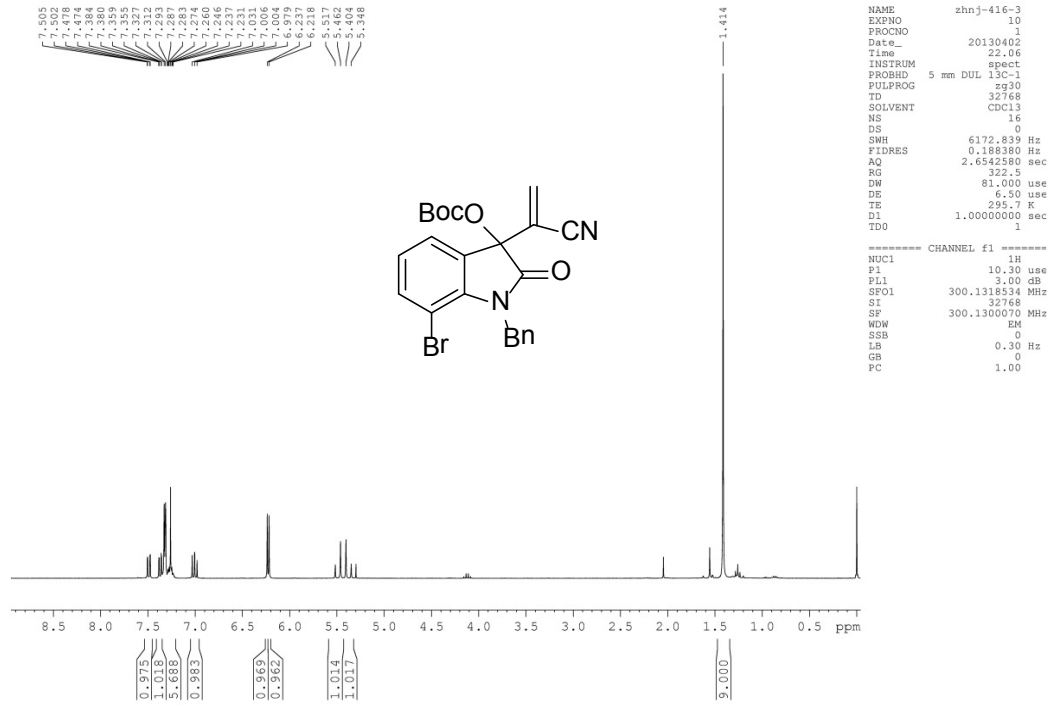

171.04
150.10
148.88
143.98
134.28
133.78
129.06
128.26
128.03
125.70
119.69
118.78
114.48
110.17
85.51
78.36
45.01
27.55
NAME zhnj-9
EXPNO 10
PROCNO 1
Date_ 20130704
Time 10.29
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 1625.5
DW 27.800 usec
DE 6.50 usec
TE 300.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

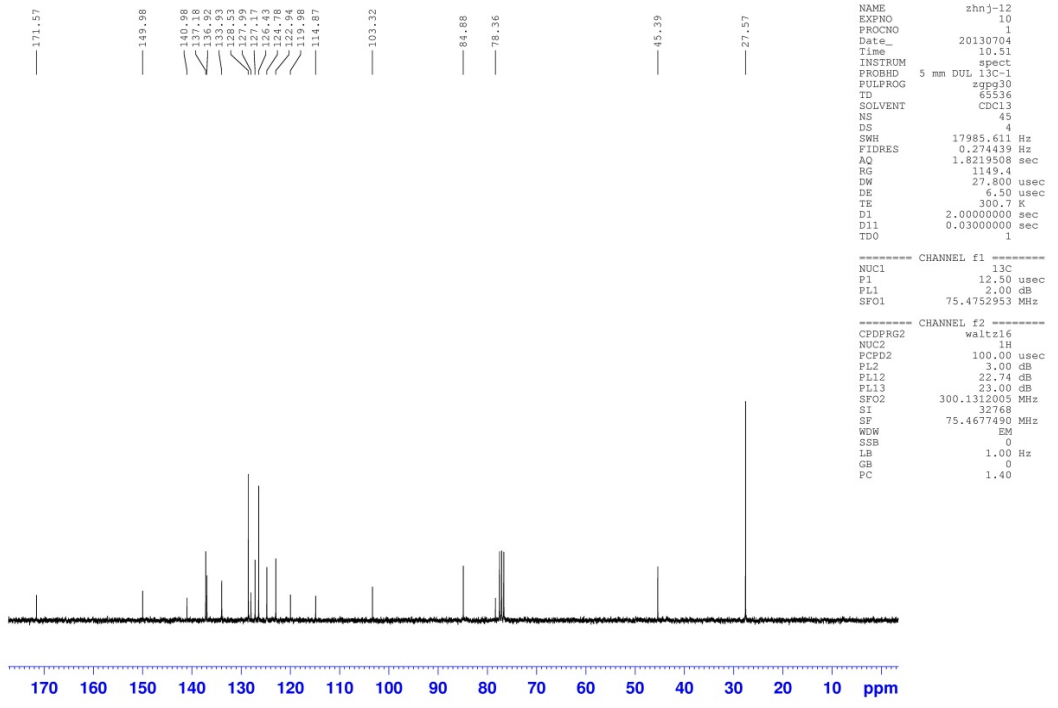

7.350
7.324
7.322
7.313
7.305
7.288
7.270
7.259
7.249
7.242
7.229
7.055
6.880
6.272
6.197
5.199
2.282
2.203
1.428
BocO
CN
O
N
Bn
NAME zhnj-416-4
EXPNO 10
PROCNO 1
Date_ 20130402
Time 22.01
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 use
DE 6.50 use
TE 296.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 use
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.602
0.969
0.972
0.999
0.986
1.976
3.001
2.933
9.000

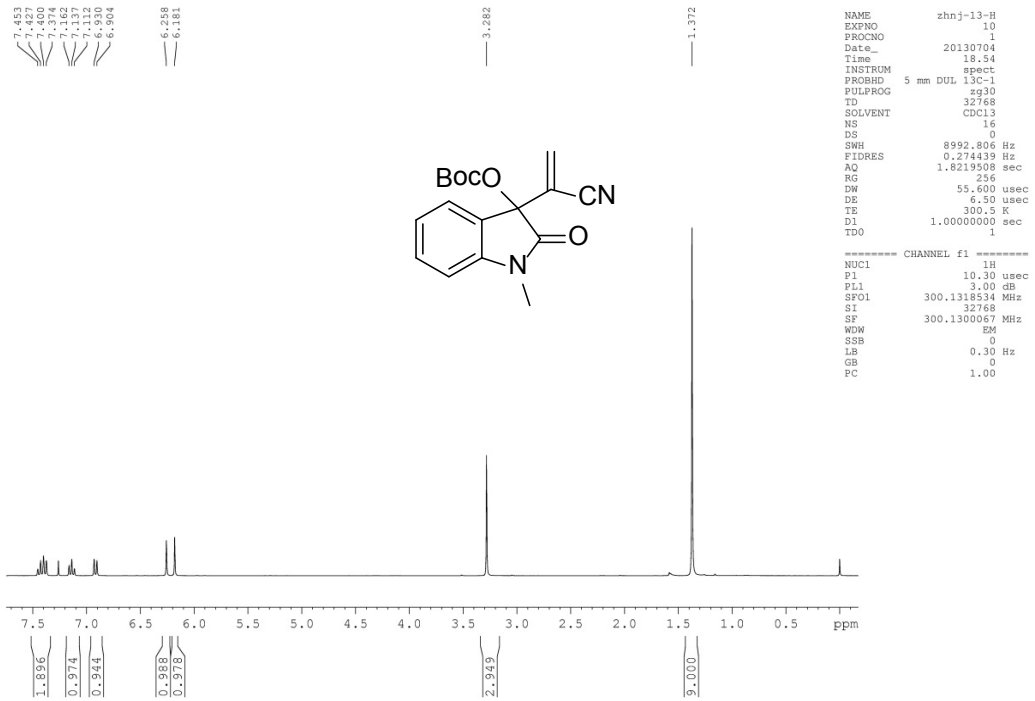

171.73
150.05
138.92
137.26
135.74
133.76
133.16
128.83
127.24
125.87
125.52
123.31
120.88
120.51
115.26
84.29
79.10
45.77
27.64
20.72
18.55
NAME zhnj-10
EXPNO 10
PROCNO 1
Date_ 20130704
Time 10.37
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 47
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 574.7
DW 27.800 usec
DE 6.50 usec
TE 300.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.405
7.381
7.342
7.334
7.328
7.321
7.313
7.308
7.294
7.288
7.282
7.277
7.271
7.258
7.247
7.236
7.209
7.202
7.197
7.182
7.175
7.180
7.117
7.096
7.090
7.067
7.055
7.050
7.040
6.223
6.202
5.104
1.407
BocO
CN
O
N
Bn
F
NAME zhnj-418-2
EXPNO 10
PROCNO 1
Date_ 20130407
Time 20.27
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 295.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.330
0.916
1.893
1.006
0.986
1.971
9.000


170.55
150.03
149.21
145.95
136.20
133.75
130.16
130.03
128.53
127.68
127.50
127.49
124.46
124.38
119.98
119.78
119.74
119.66
119.40
114.83
84.78
78.96
46.16
46.10
27.55
NAME zhnj-11
EXPNO 10
PROCNO 1
Date_ 20130704
Time 10.43
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 82
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 1625.5
DW 27.800 usec
DE 6.50 usec
TE 300.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

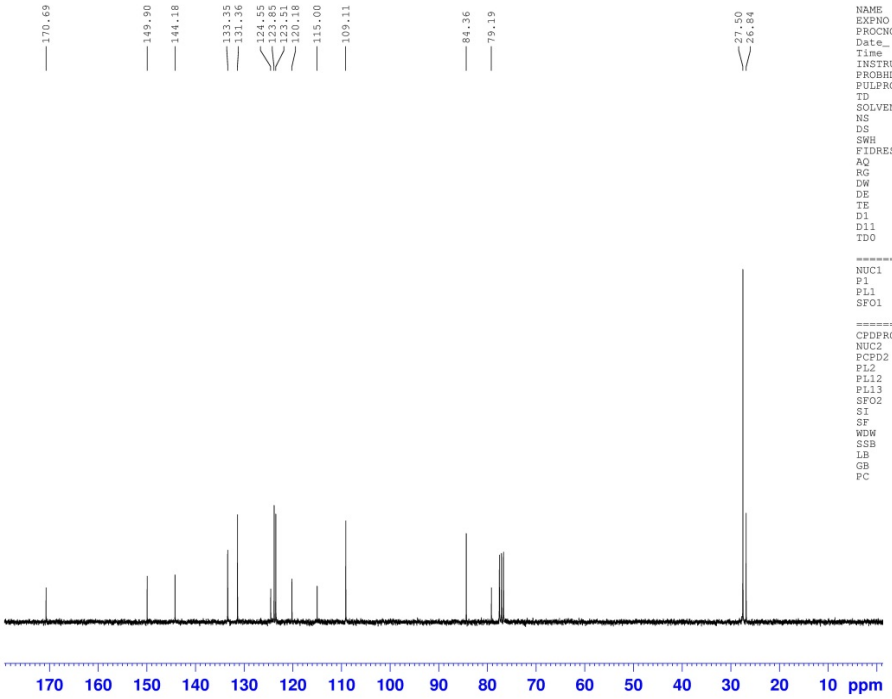

7.505
7.502
7.478
7.474
7.384
7.380
7.359
7.355
7.327
7.323
7.293
7.287
7.283
7.274
7.260
7.246
7.237
7.231
7.031
7.006
7.004
6.979
6.237
6.218
5.517
5.462
5.404
5.348
1.414
BocO
CN
O
N
Bn
Br
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.975
1.018
5.688
0.983
0.969
0.962
1.014
1.017
9.000
NAME zhnj-416-3
EXPNO 10
PROCNO 1
Date_ 20130402
Time 22.06
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 322.5
DW 81.000 use
DE 6.50 use
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 use
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300070 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


171.57
149.98
140.98
137.18
136.92
133.93
128.53
127.99
127.17
126.43
124.78
122.94
119.88
114.87
103.32
84.88
78.36
45.39
27.57
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
NAME zhnj-12
EXPNO 10
PROCNO 1
Date_ 20130704
Time 10.51
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 45
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 1149.4
DW 27.800 usec
DE 6.50 usec
TE 300.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
NAME            zhnj-13-H
EXPNO                  10
PROCNO                  1
Date_            20130704
Time                18.54
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8992.806 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                    256
DW                55.600 usec
DE                 6.50 usec
TE                300.5 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1          300.1318534 MHz
SI                  32768
SF            300.1300067 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

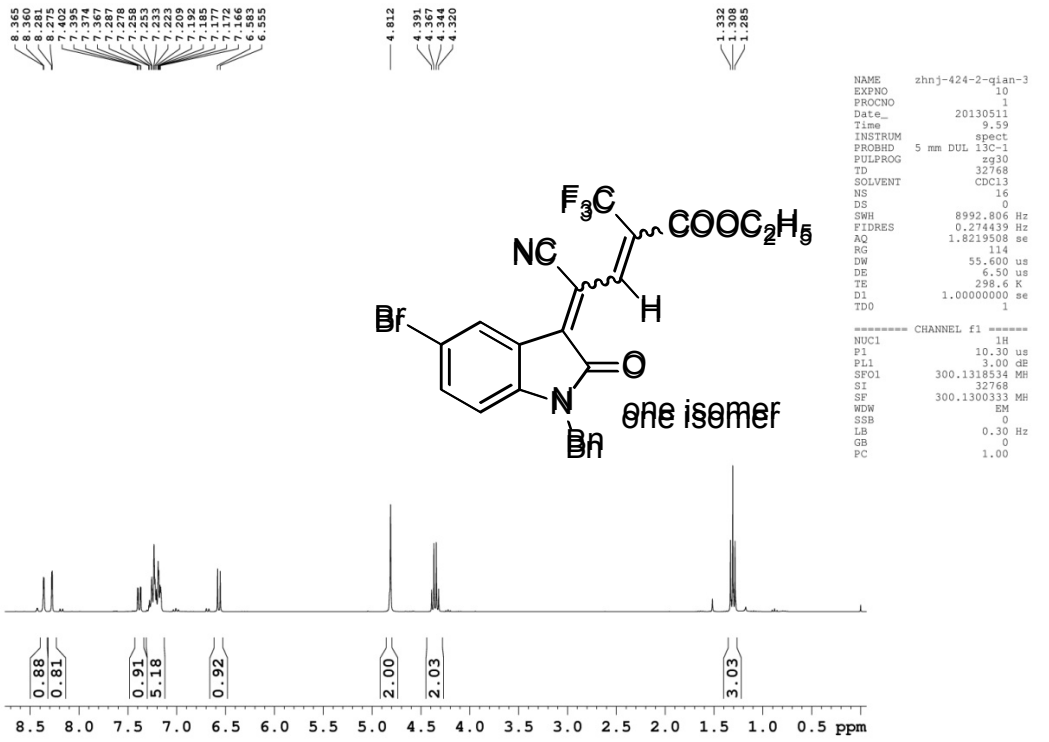



```
NAME            zhnj-13
EXPNO                  10
PROCNO                  1
Date_            20130704
Time                10.59
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     36
DS                      4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                    512
DW                27.800 usec
DE                 6.50 usec
TE                300.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

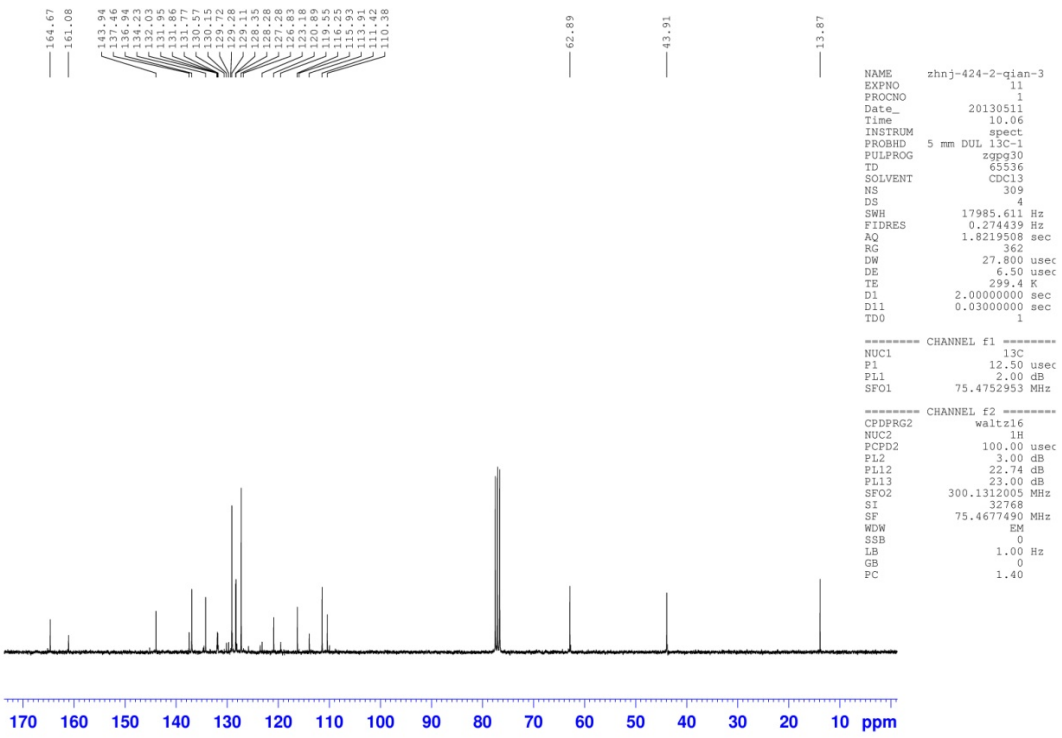
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2          300.1312005 MHz
SI                  32768
SF            75.4677490 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
```

9.2 NMR Spectra of Products




```
NAME        zhnj-424-2-qian-3
EXPNO                      10
PROCNO                      1
Date_                20130511
Time                     9.59
INSTRUM                 spect
PROBHD    5 mm DUL 13C-1
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         0
SWH                8992.806 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 se
RG                       114
DW                    55.600 us
DE                     6.50 us
TE                    298.6 K
D1                 1.00000000 se
TD0                        1

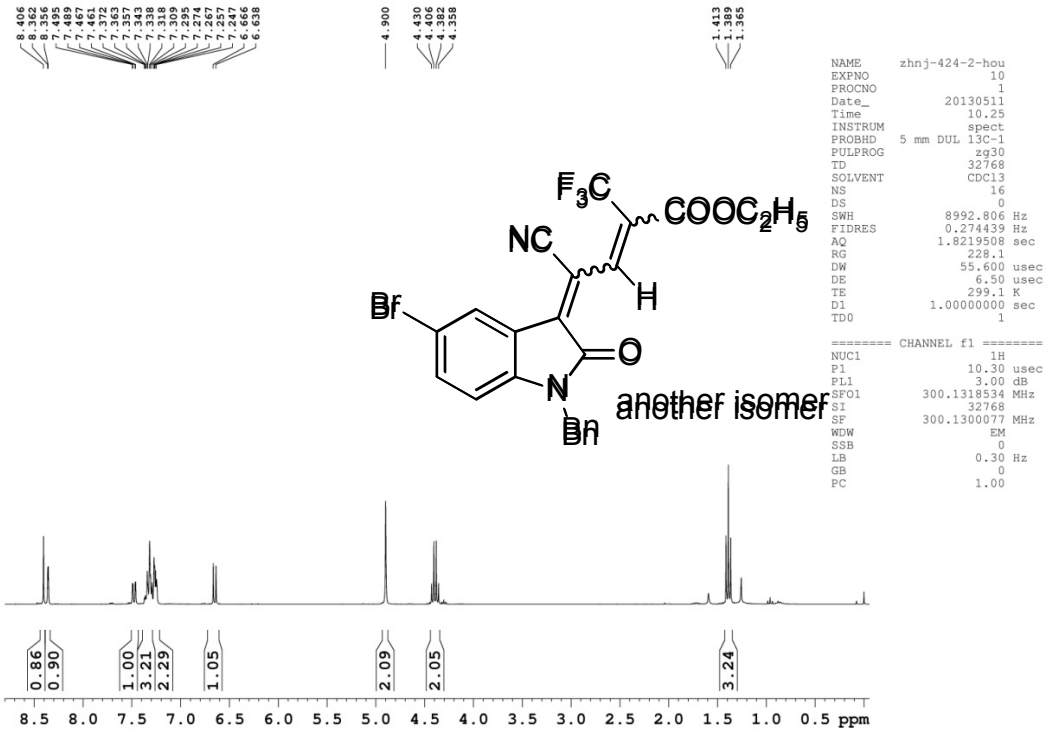
======== CHANNEL f1 ======
NUC1                      1H
P1                     10.30 us
PL1                     3.00 dB
SFO1           300.1318534 MH
SI                     32768
SF             300.1300333 MH
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

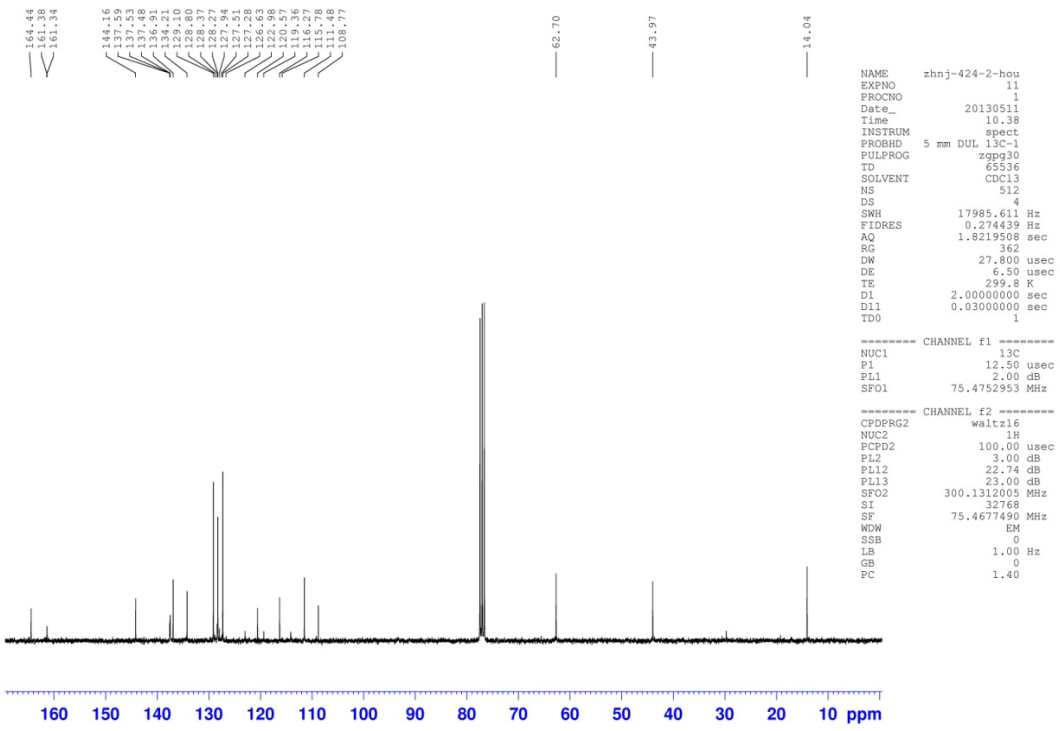


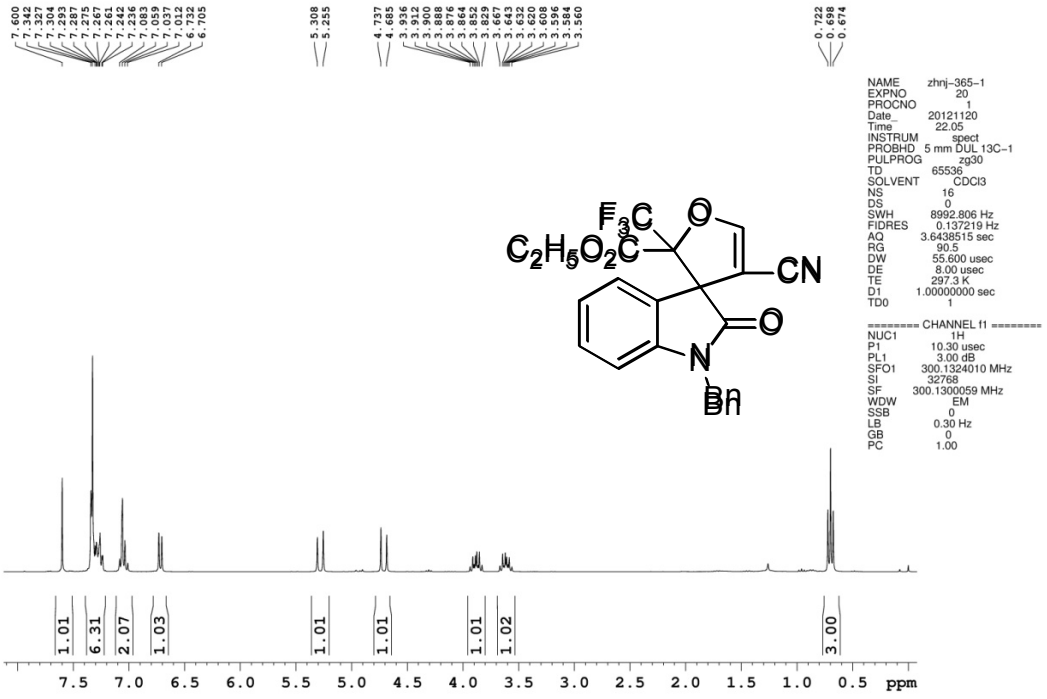

```
NAME        zhnj-424-2-qian-3
EXPNO                      11
PROCNO                      1
Date_                20130511
Time                    10.06
INSTRUM                 spect
PROBHD    5 mm DUL 13C-1
PULPROG                 zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       309
DS                         4
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                       362
DW                    27.800 usec
DE                     6.50 usec
TE                    299.4 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

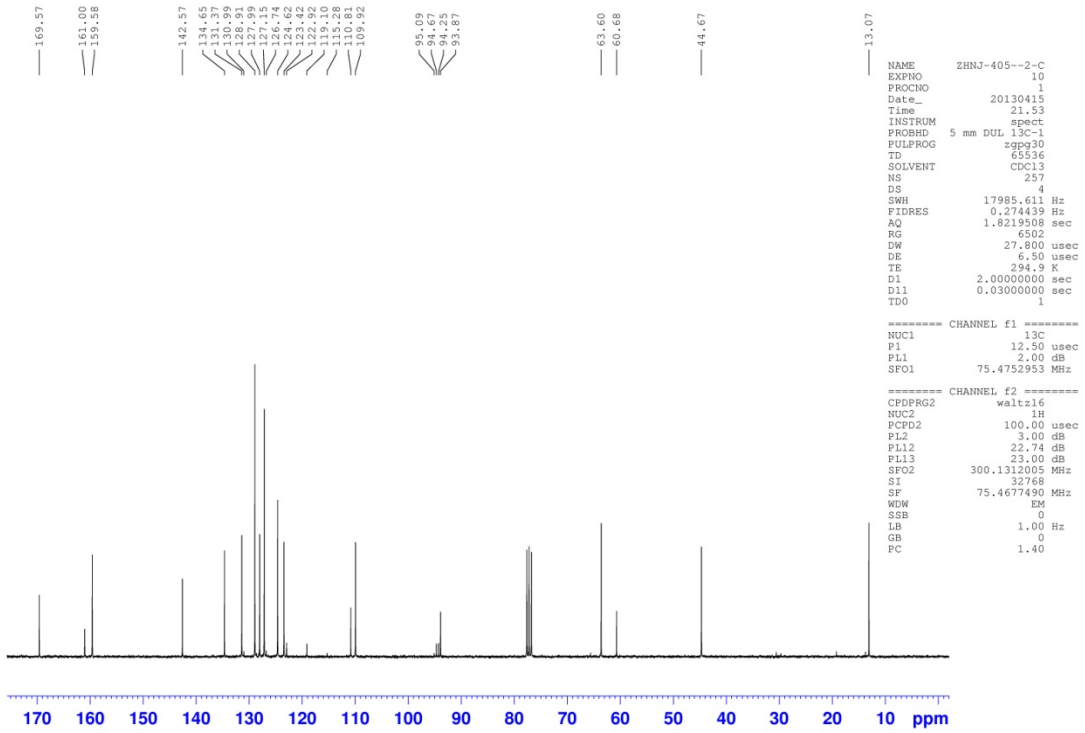
======== CHANNEL f1 ========
NUC1                      13C
P1                     12.50 usec
PL1                     2.00 dB
SFO1           75.4752953 MHz

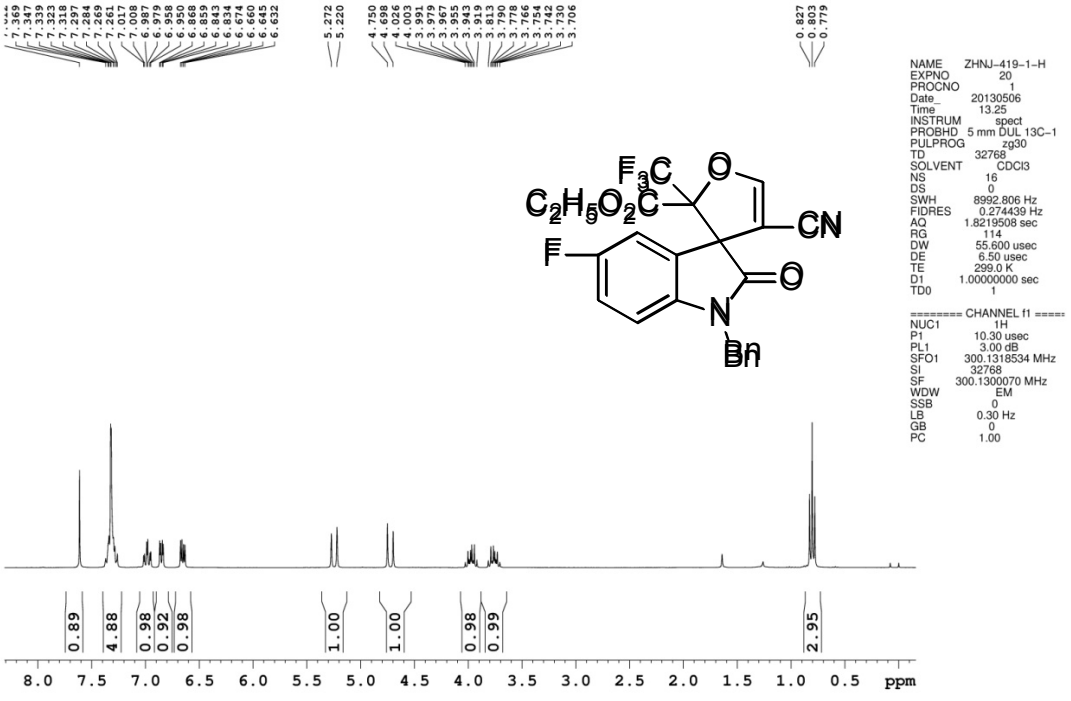
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                 100.00 usec
PL2                     3.00 dB
PL12                   22.74 dB
PL13                   23.00 dB
SFO2           300.1312005 MHz
SI                     32768
SF             75.4677490 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

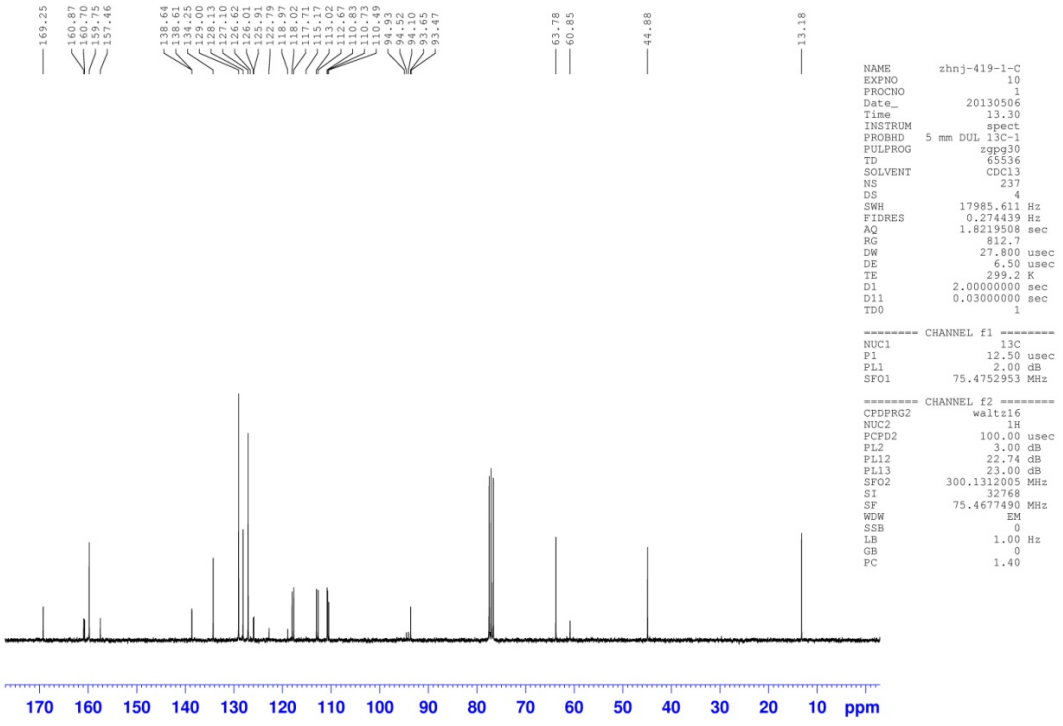

8.406
8.362
8.356
7.485
7.480
7.467
7.461
7.372
7.363
7.357
7.343
7.338
7.318
7.309
7.295
7.274
7.257
7.247
6.666
6.638
4.900
4.430
4.406
4.382
4.358
1.413
1.389
1.365
F3C
COOC2H5
NC
H
Br
O
N
Bn
another isomer
NAME zhnj-424-2-hou
EXPNO 10
PROCNO 1
Date_ 20130511
Time 10.25
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 228.1
DW 55.600 usec
DE 6.50 usec
TE 299.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.86
0.90
1.00
3.21
2.29
1.05
2.09
2.05
3.24
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

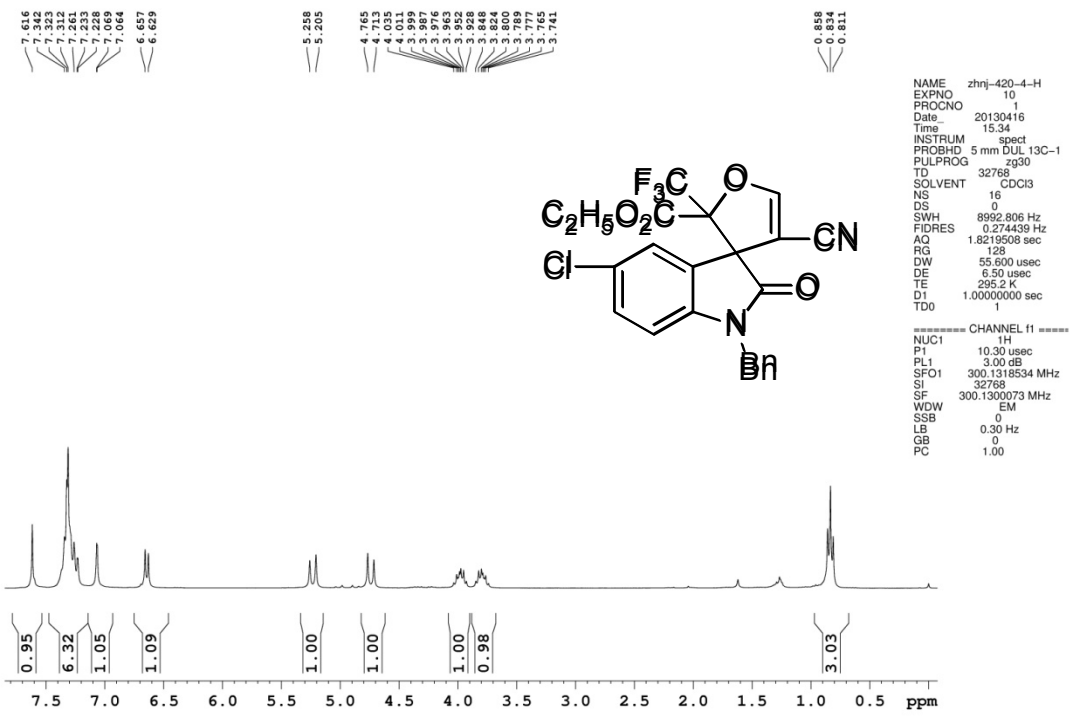

164.44
161.38
161.34
144.16
137.59
137.53
137.48
136.91
134.21
129.10
128.80
128.37
128.27
127.94
127.51
127.28
126.63
126.58
120.37
119.36
116.27
115.78
111.48
108.77
62.70
43.97
14.04
NAME zhnj-424-2-hou
EXPNO 11
PROCNO 1
Date_ 20130511
Time 10.38
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 362
DW 27.800 usec
DE 6.50 usec
TE 299.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

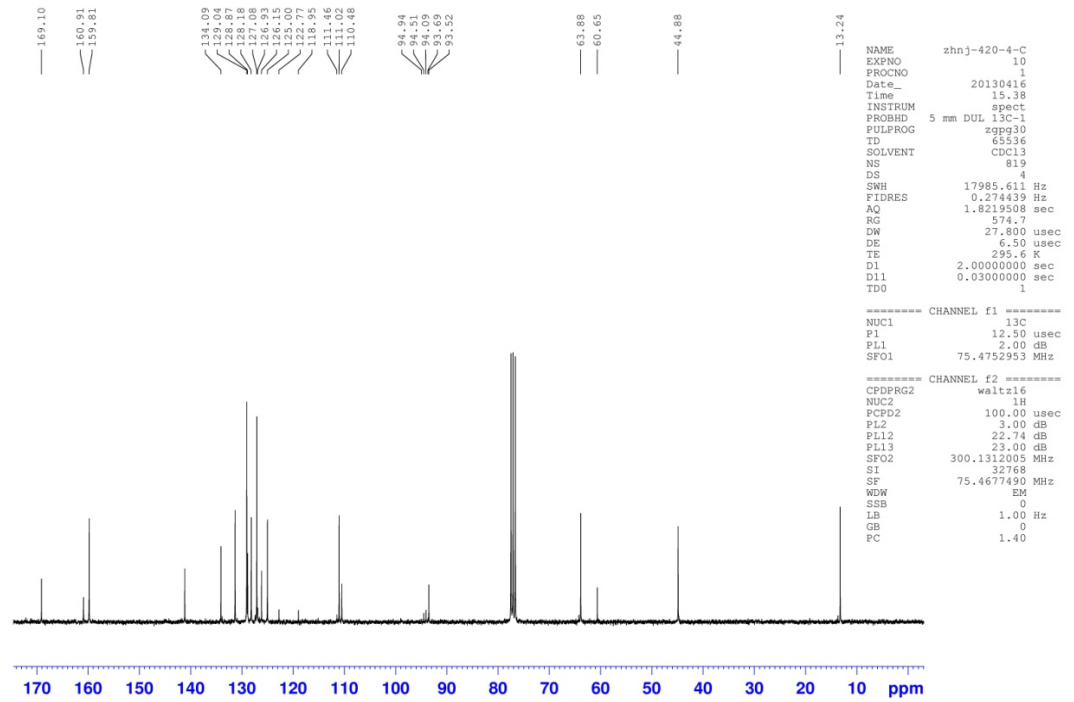

7.600
7.342
7.327
7.304
7.295
7.287
7.275
7.267
7.261
7.242
7.236
7.083
7.059
7.037
7.012
6.732
6.705
5.308
5.255
4.737
4.685
3.936
3.912
3.900
3.888
3.876
3.864
3.852
3.829
3.667
3.643
3.632
3.620
3.608
3.596
3.584
3.560
0.722
0.698
0.674
NAME zhnj-365-1
EXPNO 20
PROCNO 1
Date_ 20121120
Time 22.05
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 90.5
DW 55.600 usec
DE 8.00 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1324010 MHz
SI 32768
SF 300.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F3C
O
C2H5O2C
CN
O
N
Bn
1.01
6.31
2.07
1.03
1.01
1.01
1.01
1.02
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

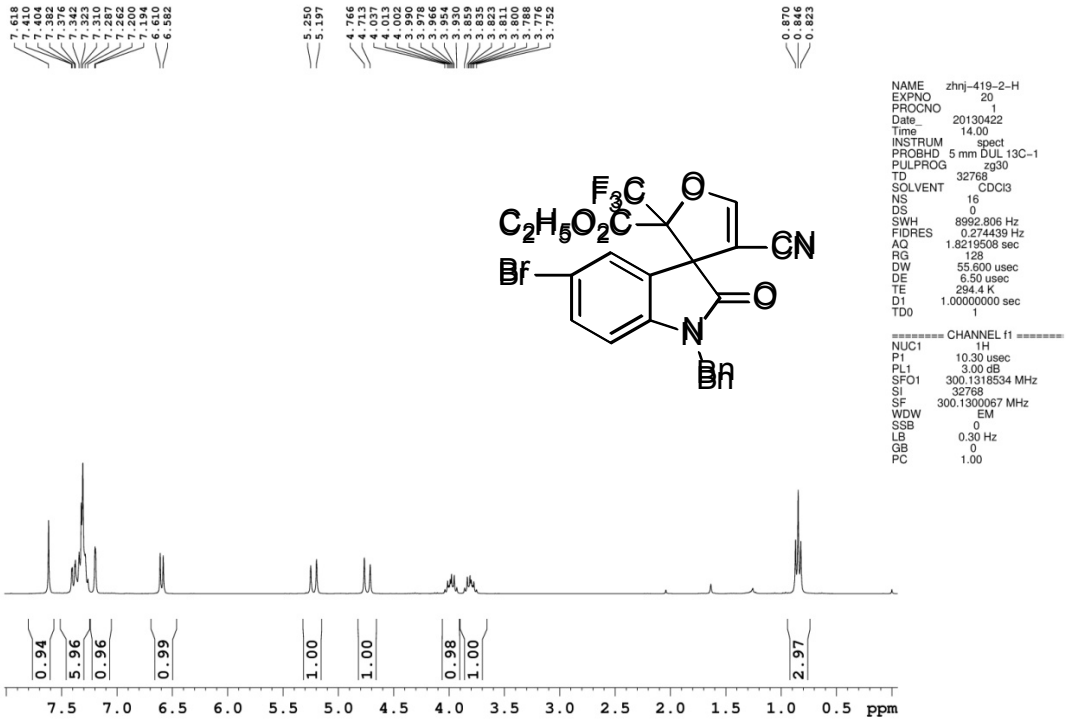

169.57
161.00
159.58
142.57
134.65
131.37
130.99
128.91
127.99
127.15
126.74
124.42
123.62
122.92
119.10
115.28
110.81
109.92
95.09
94.67
94.25
93.87
63.60
60.68
44.67
13.07
NAME ZHNJ-405--2-C
EXPNO 10
PROCNO 1
Date_ 20130415
Time 21.53
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 257
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 6502
DW 27.800 usec
DE 6.50 usec
TE 294.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

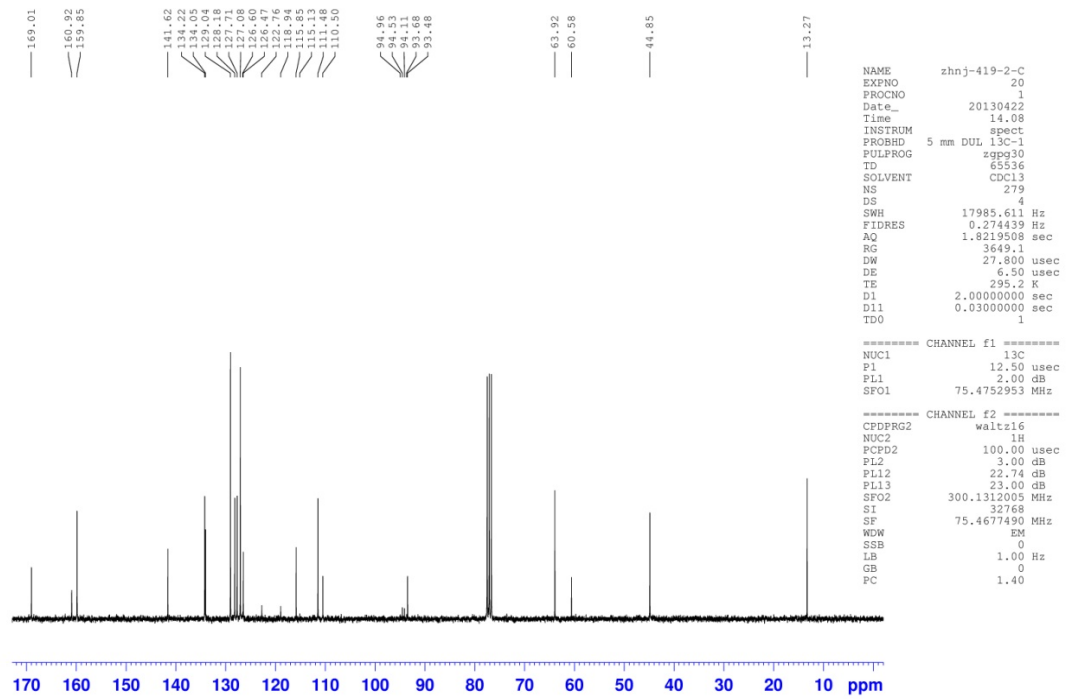

7.369
7.347
7.339
7.323
7.318
7.297
7.284
7.269
7.261
7.017
7.008
6.987
6.979
6.958
6.950
6.868
6.859
6.843
6.834
6.674
6.660
6.645
6.632
5.272
5.220
4.750
4.698
4.026
4.003
3.991
3.979
3.967
3.955
3.943
3.919
3.813
3.790
3.778
3.766
3.754
3.742
3.730
3.706
0.827
0.803
0.779
F3C
O
C2H5O2C
CN
F
O
N
Bn
NAME ZHNJ-419-1-H
EXPNO 20
PROCNO 1
Date_ 20130506
Time 13.25
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 114
DW 55.600 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300070 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.89
4.88
0.98
0.92
0.98
1.00
1.00
0.98
0.99
2.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

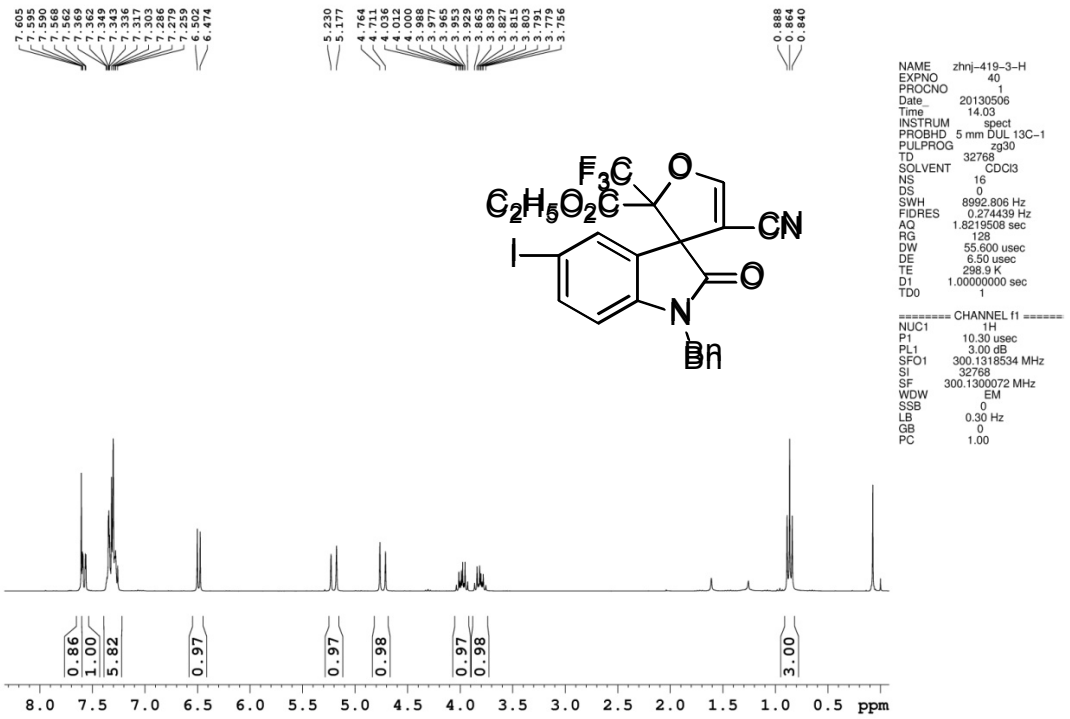

169.25
160.87
160.70
159.75
157.46
138.64
138.61
134.25
129.00
128.13
127.10
126.62
126.01
125.91
125.79
118.97
118.02
117.71
115.17
113.02
112.87
110.83
110.73
110.49
94.93
94.52
94.10
93.65
93.47
63.78
60.85
44.88
13.18
NAME zhnj-419-1-C
EXPNO 10
PROCNO 1
Date_ 20130506
Time 13.30
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 237
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 812.7
DW 27.800 usec
DE 6.50 usec
TE 299.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

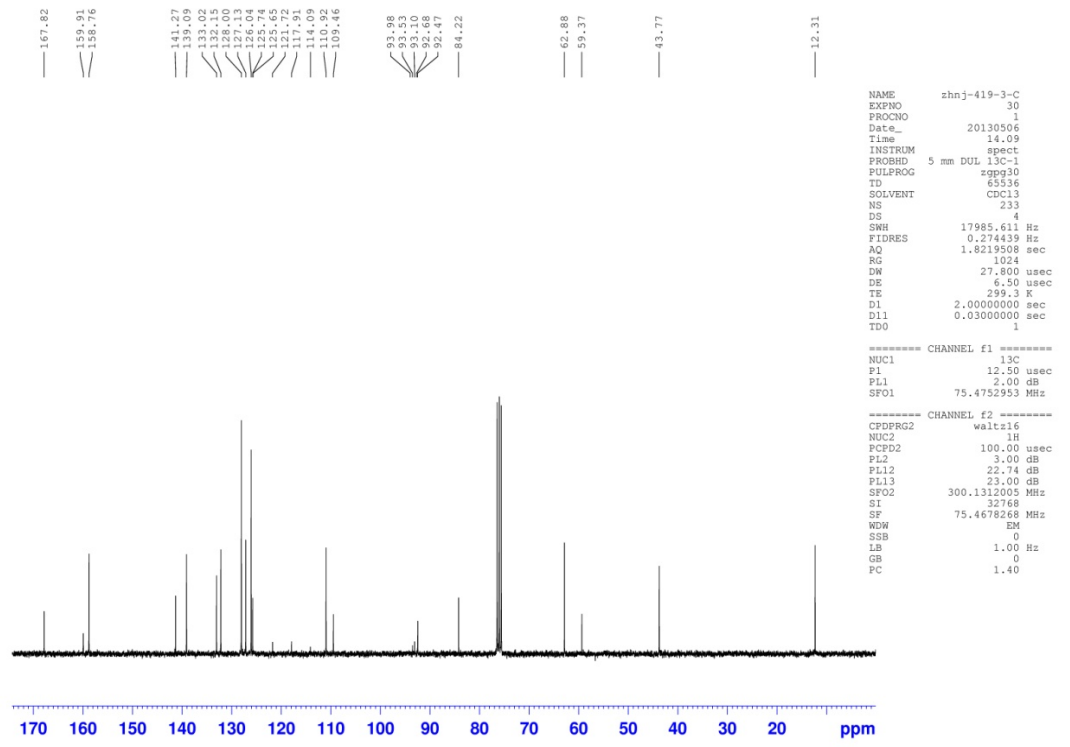

7.616
7.342
7.323
7.312
7.261
7.233
7.228
7.069
7.064
6.657
6.629
5.258
5.205
4.765
4.713
4.035
4.011
3.999
3.987
3.976
3.965
3.952
3.928
3.848
3.824
3.800
3.789
3.777
3.765
3.741
0.858
0.834
0.811
NAME zhnj-420-4-H
EXPNO 10
PROCNO 1
Date_ 20130416
Time 15.34
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 128
DW 55.600 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.95
6.32
1.05
1.09
1.00
1.00
1.00
0.98
3.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

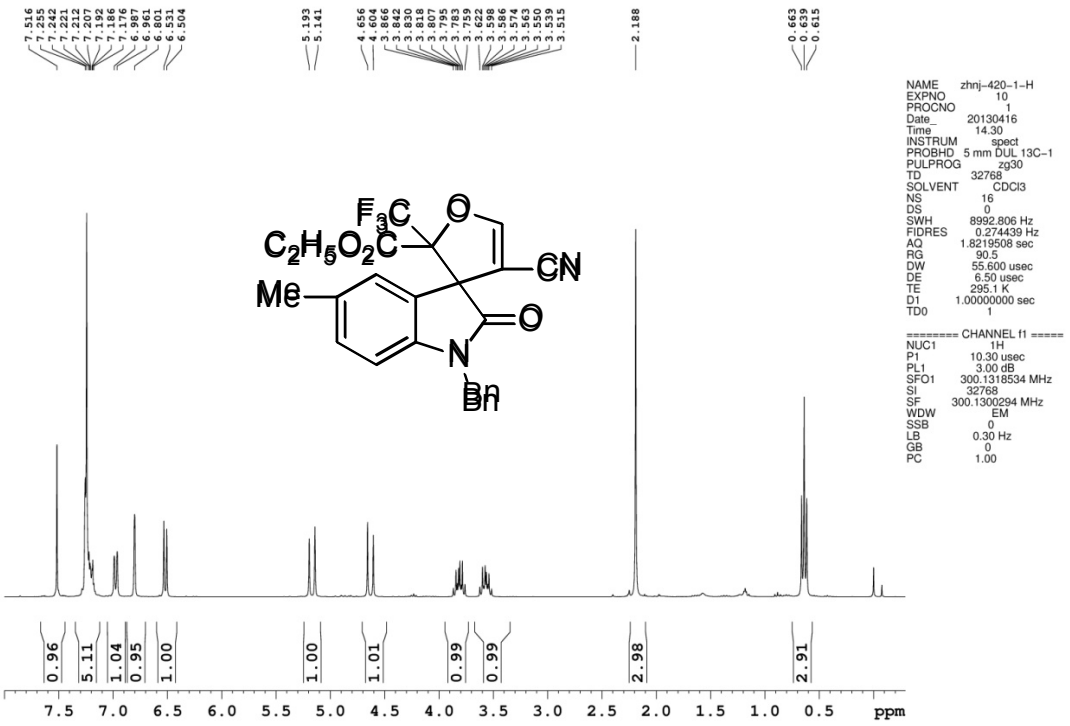

169.10
160.91
159.81
134.09
129.04
128.87
128.18
127.08
126.93
126.15
125.00
122.77
118.95
111.46
111.02
110.48
94.94
94.51
94.09
93.69
93.52
63.88
60.65
44.88
13.24
NAME zhnj-420-4-C
EXPNO 10
PROCNO 1
Date_ 20130416
Time 15.38
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 819
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 574.7
DW 27.800 usec
DE 6.50 usec
TE 295.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

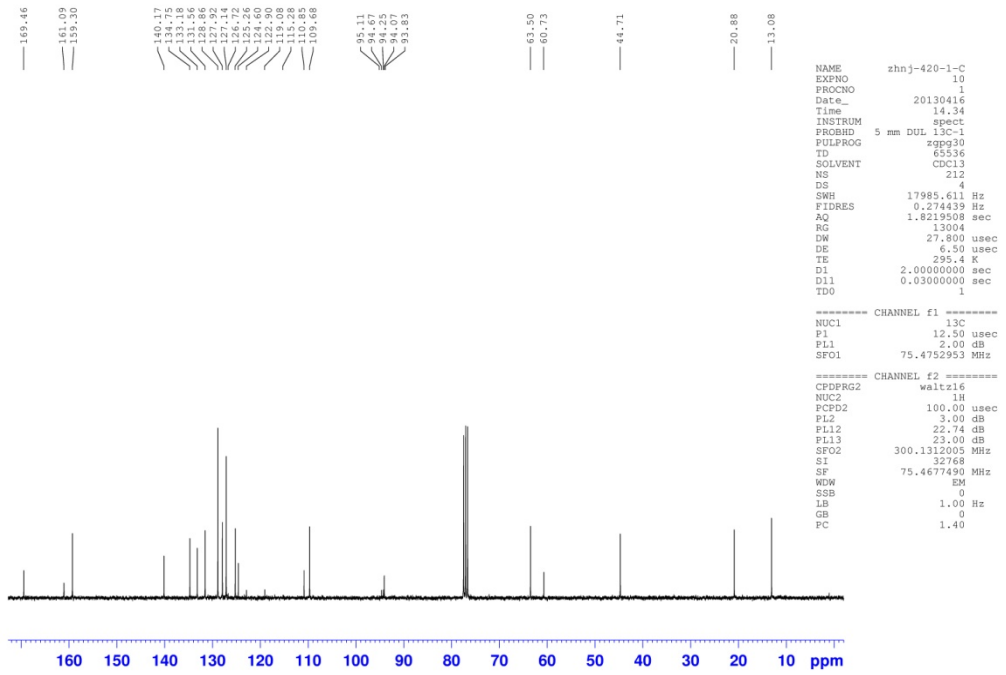

7.618
7.410
7.404
7.382
7.376
7.342
7.323
7.310
7.287
7.262
7.200
7.194
6.610
6.582
5.250
5.197
4.766
4.753
4.737
4.037
4.013
4.002
3.990
3.978
3.966
3.954
3.930
3.859
3.835
3.823
3.811
3.800
3.788
3.776
3.752
0.870
0.846
0.823
NAME zhnj-419-2-H
EXPNO 20
PROCNO 1
Date_ 20130422
Time 14.00
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 128
DW 55.600 usec
DE 6.50 usec
TE 294.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.94
5.96
0.96
0.99
1.00
1.00
0.98
1.00
2.97
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

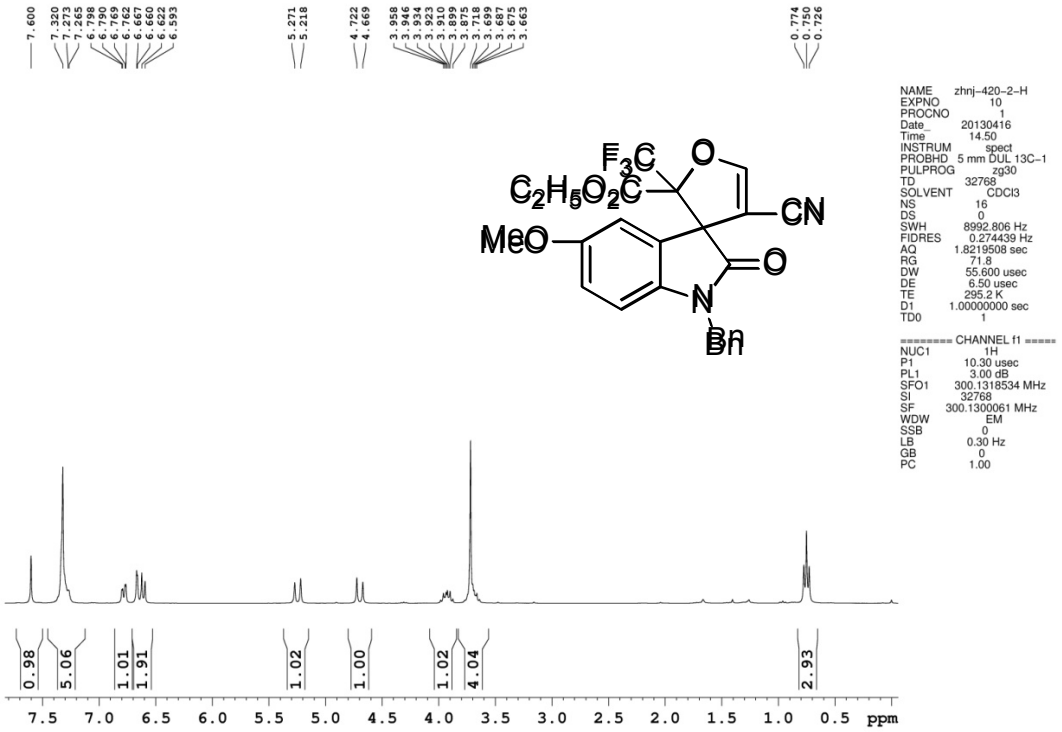

169.01
160.92
159.85
141.62
138.22
134.25
129.04
128.18
127.71
127.08
126.60
126.47
126.26
118.94
115.85
115.13
111.48
110.50
94.96
94.53
94.11
93.60
93.48
63.92
60.58
44.85
13.27
NAME zhnj-419-2-C
EXPNO 20
PROCNO 1
Date_ 20130422
Time 14.08
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 279
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 3649.1
DW 27.800 usec
DE 6.50 usec
TE 295.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

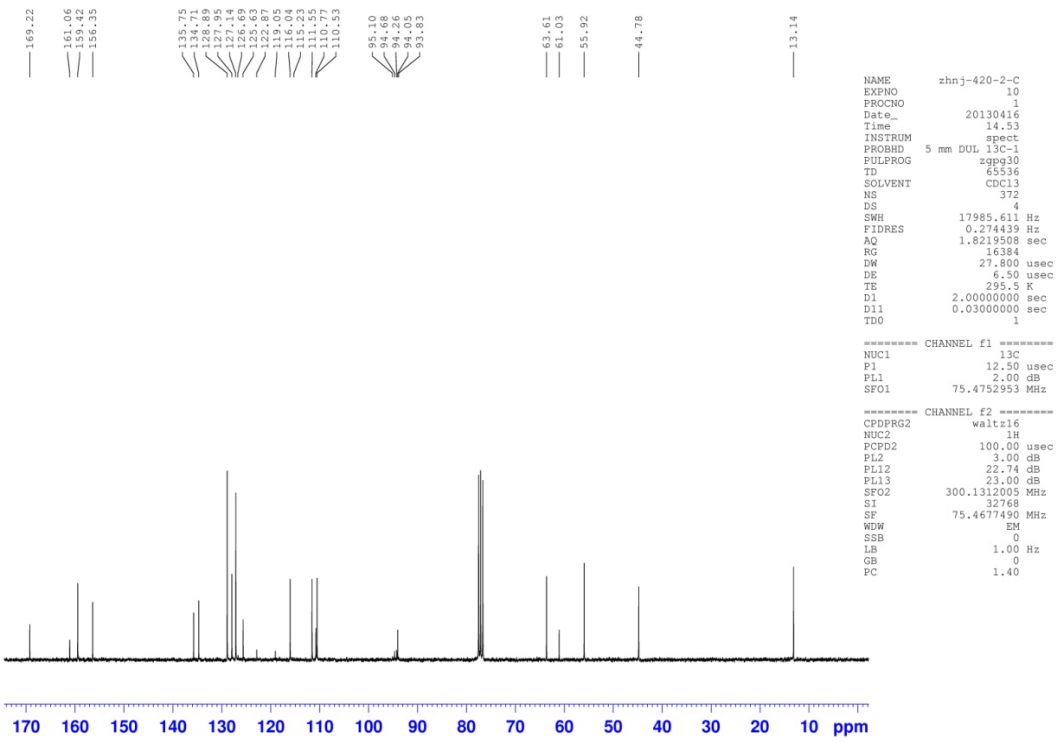

7.605
7.595
7.590
7.568
7.562
7.369
7.362
7.349
7.343
7.316
7.317
7.303
7.286
7.279
7.259
6.502
6.474
5.230
5.177
4.764
4.711
4.036
4.012
4.000
3.988
3.977
3.965
3.953
3.929
3.863
3.839
3.827
3.815
3.803
3.791
3.779
3.756
0.888
0.864
0.840
NAME zhnj-419-3-H
EXPNO 40
PROCNO 1
Date_ 20130506
Time 14.03
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 128
DW 55.600 usec
DE 6.50 usec
TE 298.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F3C
O
C2H5O2C
CN
I
O
N
Bn
0.86
1.00
5.82
0.97
0.97
0.98
0.97
0.98
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

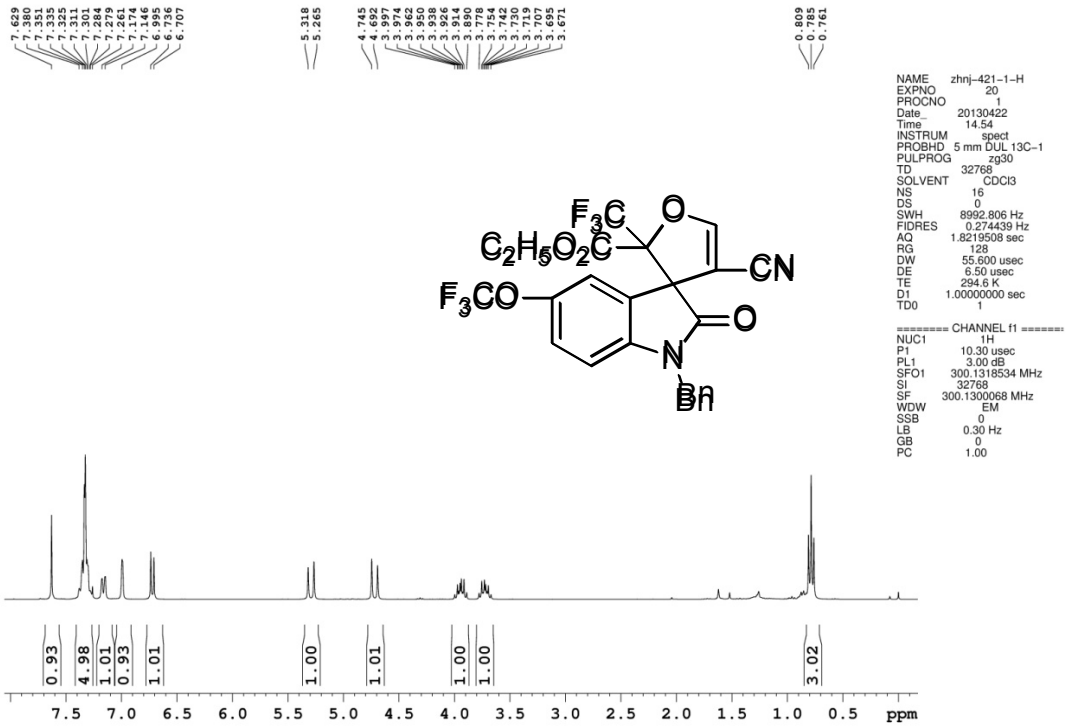

167.82
159.91
158.76
141.27
139.09
133.02
132.15
128.00
127.13
126.04
125.74
125.65
121.72
117.91
114.09
110.92
109.46
83.98
83.55
93.10
92.68
92.47
84.22
62.88
59.37
43.77
12.31
NAME zhnj-419-3-C
EXPNO 30
PROCNO 1
Date_ 20130506
Time 14.09
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 233
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 1024
DW 27.800 usec
DE 6.50 usec
TE 299.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4678268 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

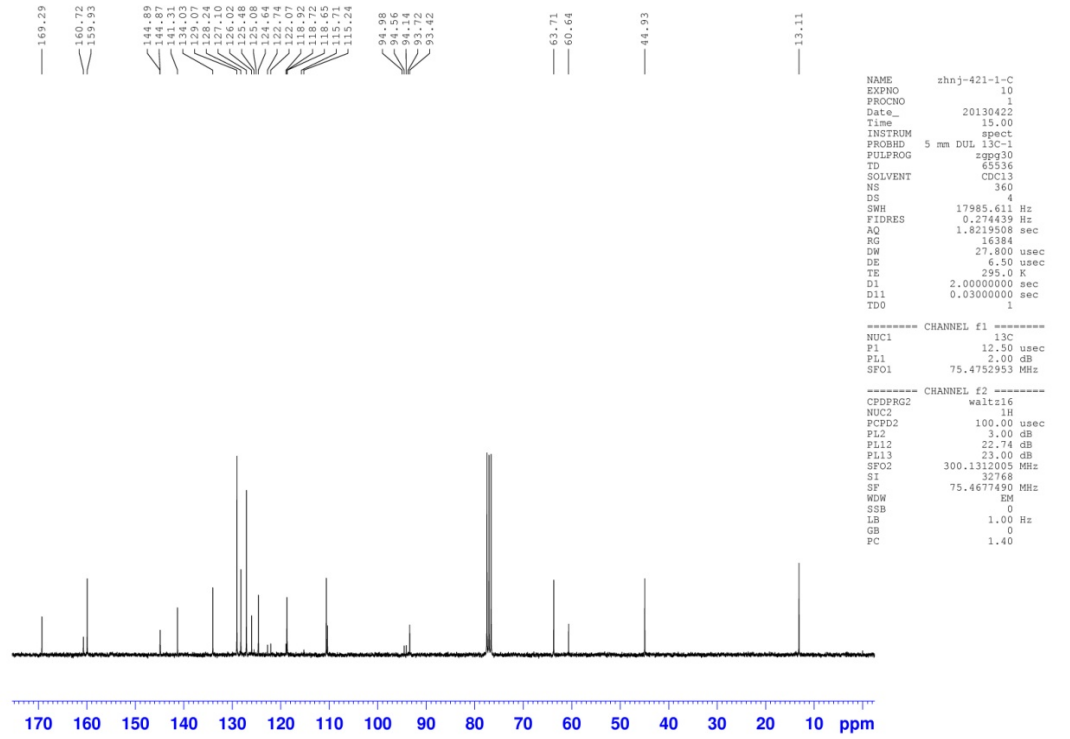

7.516
7.355
7.242
7.221
7.212
7.207
7.192
7.186
7.176
6.987
6.961
6.801
6.531
6.504
5.193
5.141
4.656
4.604
3.866
3.842
3.830
3.818
3.807
3.795
3.783
3.759
3.622
3.598
3.586
3.574
3.563
3.550
3.539
3.515
2.188
0.663
0.639
0.615
F3C
O
C2H5O2C
CN
Me
O
N
Bn
0.96
5.11
1.04
0.95
1.00
1.00
1.01
0.99
0.99
2.98
2.91
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
NAME zhnj-420-1-H
EXPNO 10
PROCNO 1
Date_ 20130416
Time 14.30
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 90.5
DW 55.600 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300294 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

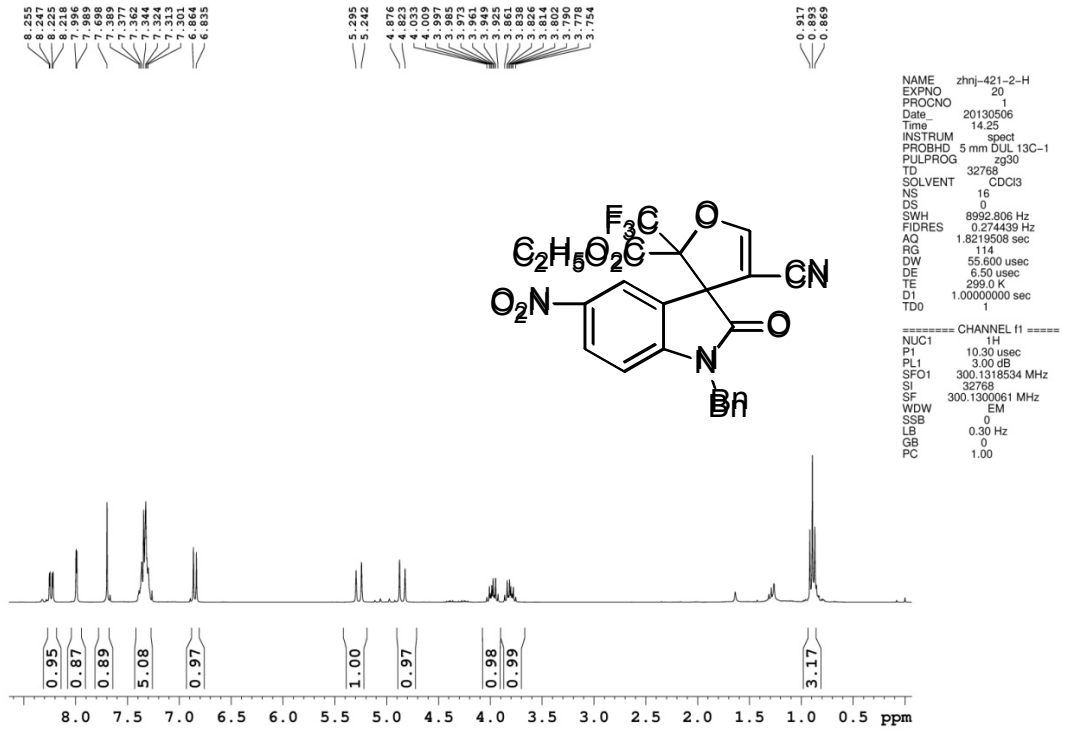

169.46
161.09
159.30
140.17
134.75
133.18
131.56
128.86
127.92
127.14
126.72
125.26
124.60
122.90
119.08
115.28
110.85
109.68
95.11
94.67
94.25
94.07
93.83
63.50
60.73
44.71
20.88
13.08
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
NAME zhnj-420-1-C
EXPNO 10
PROCNO 1
Date_ 20130416
Time 14.34
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 212
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.50 usec
TE 295.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

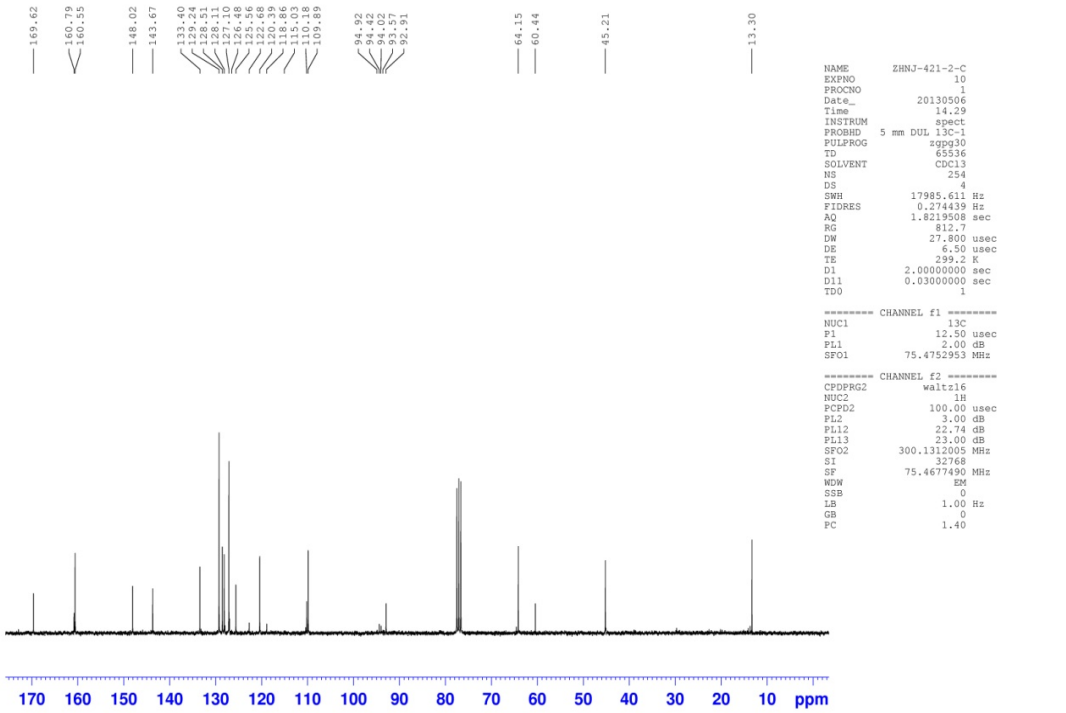

7.600
7.320
7.273
7.265
6.798
6.780
6.765
6.762
6.667
6.660
6.622
6.593
5.271
5.218
4.722
4.669
3.958
3.946
3.934
3.923
3.910
3.899
3.875
3.718
3.699
3.687
3.675
3.663
0.774
0.750
0.726
NAME zhnj-420-2-H
EXPNO 10
PROCNO 1
Date_ 20130416
Time 14.50
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 71.8
DW 55.600 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F3C
O
C2H5O2C
CN
MeO
O
N
Bn
0.98
5.06
1.01
1.91
1.02
1.00
1.02
4.04
2.93
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

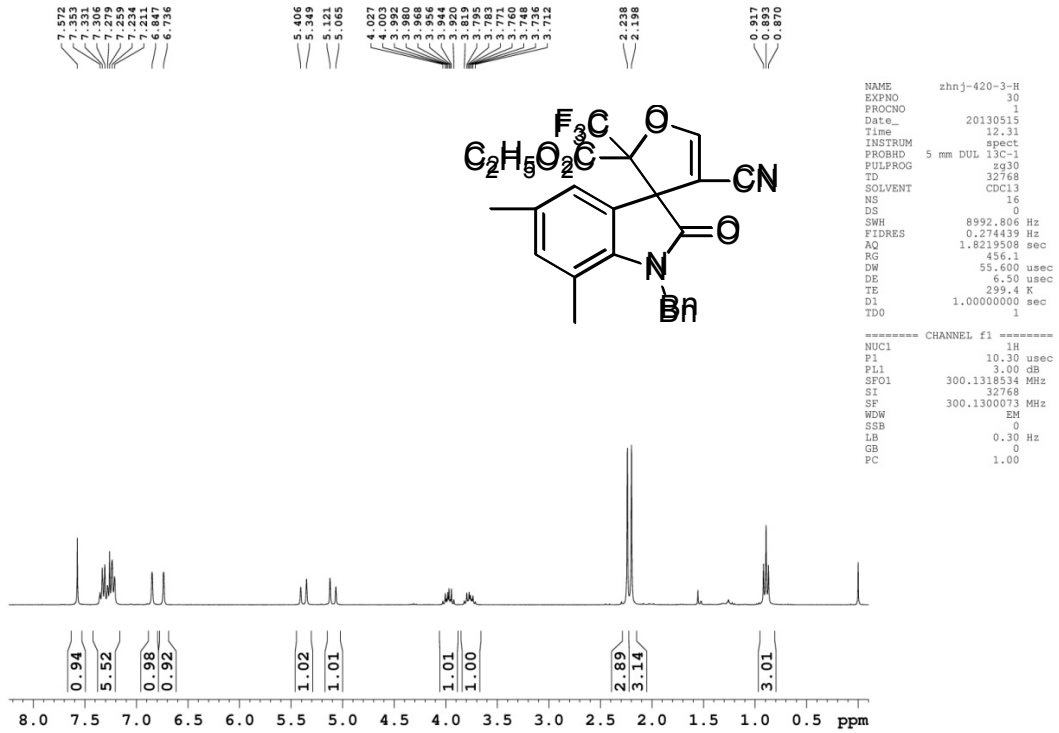

169.22
161.06
159.42
156.35
135.75
134.71
128.89
127.95
127.14
125.69
125.63
122.87
119.05
116.04
115.23
111.55
110.77
110.53
95.10
94.68
94.26
94.05
93.83
63.61
61.03
55.92
44.78
13.14
NAME zhnj-420-2-C
EXPNO 10
PROCNO 1
Date_ 20130416
Time 14.53
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 372
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 6.50 usec
TE 295.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

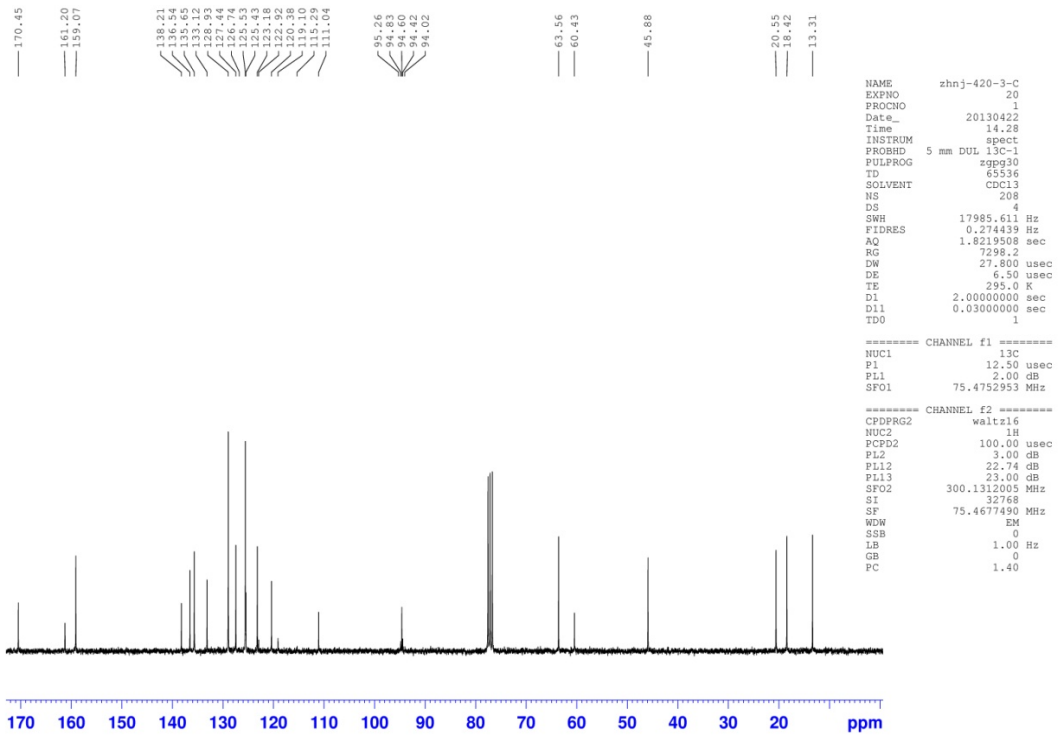

7.629
7.380
7.351
7.335
7.325
7.311
7.301
7.284
7.278
7.261
7.174
7.146
6.995
6.736
6.707
5.318
5.265
4.745
4.692
3.997
3.974
3.962
3.950
3.938
3.926
3.914
3.890
3.778
3.754
3.742
3.730
3.719
3.707
3.695
3.671
0.809
0.785
0.761
F3C
O
C2H5O2C
CN
F3CO
O
N
Bn
NAME zhnj-421-1-H
EXPNO 20
PROCNO 1
Date_ 20130422
Time 14.54
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 128
DW 55.600 usec
DE 6.50 usec
TE 294.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300068 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.93
4.98
1.01
0.93
1.01
1.00
1.01
1.00
1.00
3.02
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

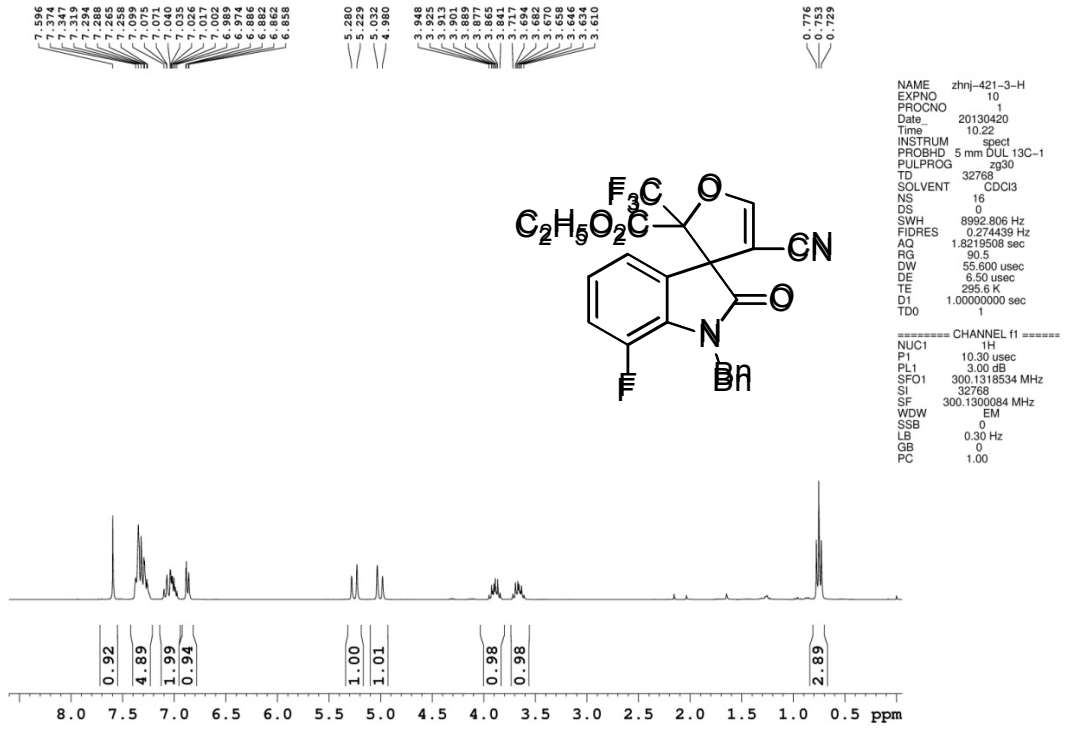

169.29
160.72
159.93
144.89
144.87
141.31
134.03
129.07
128.84
127.10
126.02
125.48
125.08
124.64
124.44
122.07
118.92
118.72
118.65
115.71
115.24
94.98
94.56
94.14
93.72
93.42
63.71
60.64
44.93
13.11
NAME zhnj-421-1-C
EXPNO 10
PROCNO 1
Date_ 20130422
Time 15.00
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 360
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 6.50 usec
TE 295.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

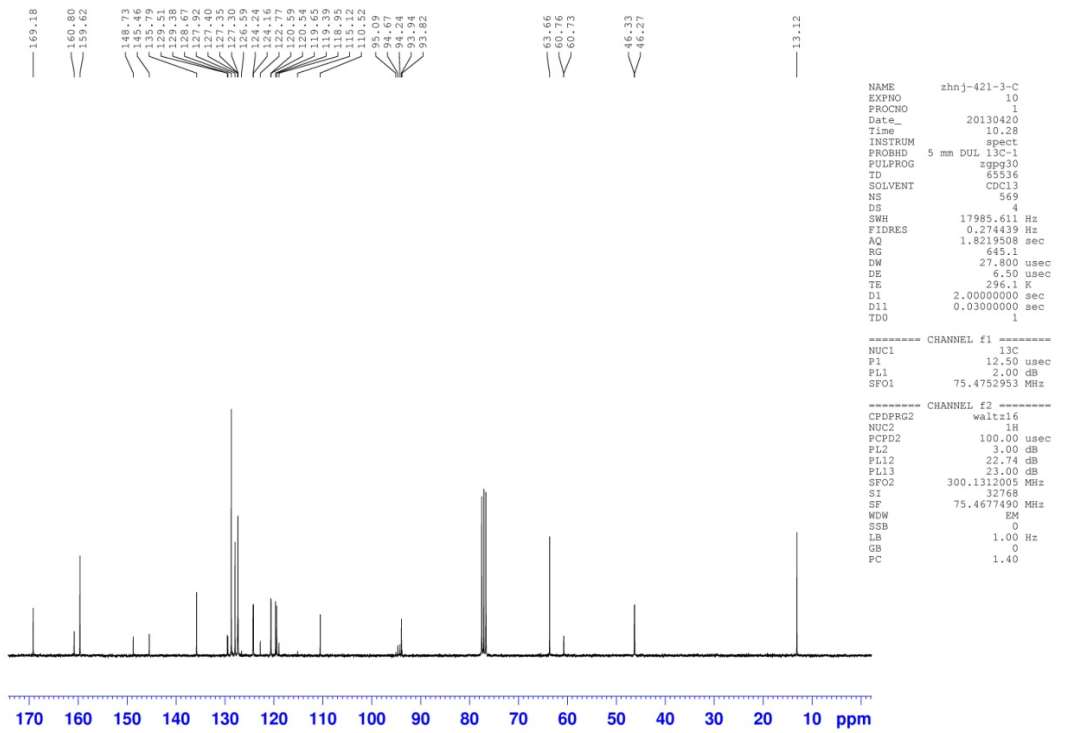

8.255
8.247
8.225
8.218
7.996
7.989
7.698
7.389
7.377
7.362
7.344
7.324
7.313
7.301
6.864
6.835
5.295
5.242
4.876
4.823
4.803
4.009
3.997
3.985
3.973
3.961
3.949
3.925
3.861
3.838
3.826
3.814
3.802
3.790
3.778
3.754
0.917
0.893
0.869
NAME zhnj-421-2-H
EXPNO 20
PROCNO 1
Date_ 20130506
Time 14.25
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 114
DW 55.600 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F3C
O
C2H5O2C
CN
O2N
O
N
Bn
0.95
0.87
0.89
5.08
0.97
1.00
0.97
0.98
0.99
3.17
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

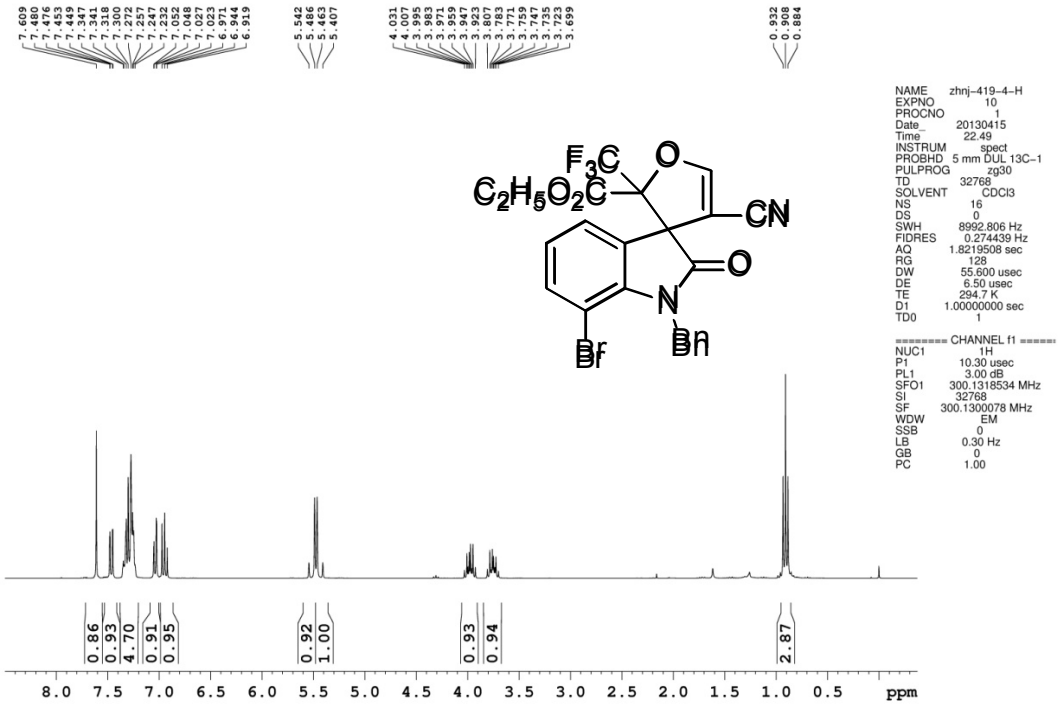

169.62
160.79
160.55
148.02
143.67
133.40
129.24
128.51
128.11
127.10
126.48
125.56
122.68
121.39
118.86
115.03
110.18
109.89
94.92
94.42
94.02
93.57
92.91
64.15
60.44
45.21
13.30
NAME ZHNJ-421-2-C
EXPNO 10
PROCNO 1
Date_ 20130506
Time 14.29
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 254
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 812.7
DW 27.800 usec
DE 6.50 usec
TE 299.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

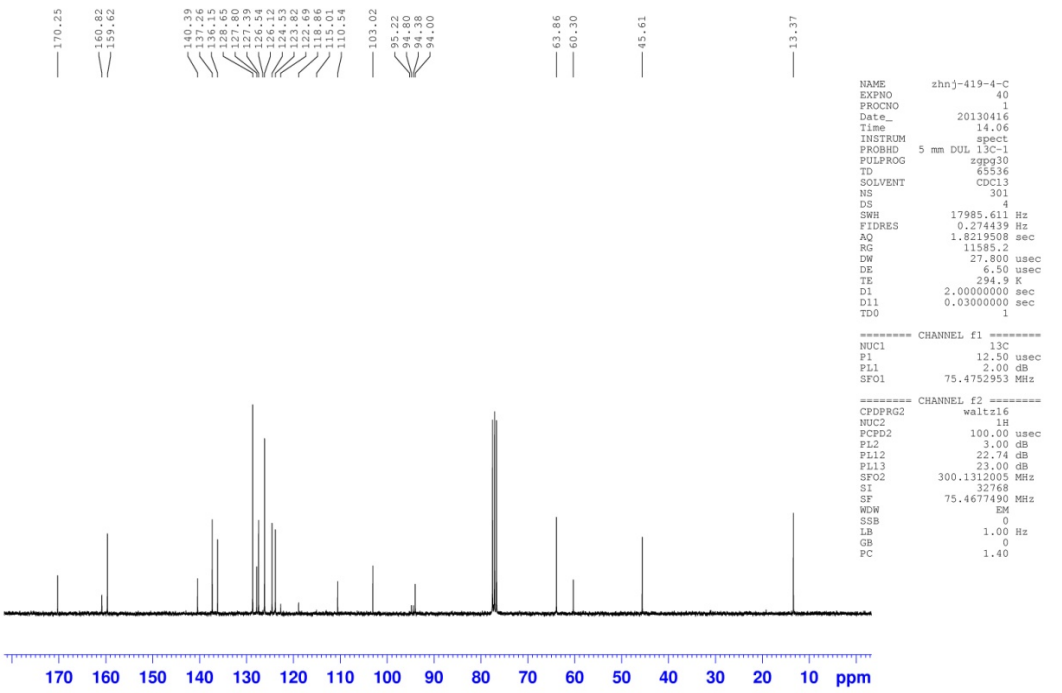

7.572
7.353
7.333
7.306
7.279
7.259
7.234
7.211
6.841
6.736
5.406
5.349
5.121
5.065
4.027
4.003
3.992
3.980
3.968
3.956
3.944
3.920
3.811
3.795
3.783
3.771
3.760
3.748
3.736
3.712
2.238
2.198
0.917
0.893
0.870
F3C
O
C2H5O2C
CN
O
N
Bn
NAME zhnj-420-3-H
EXPNO 30
PROCNO 1
Date_ 20130515
Time 12.31
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 456.1
DW 55.600 usec
DE 6.50 usec
TE 299.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.94
5.52
0.98
0.92
1.02
1.01
1.01
1.00
2.89
3.14
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

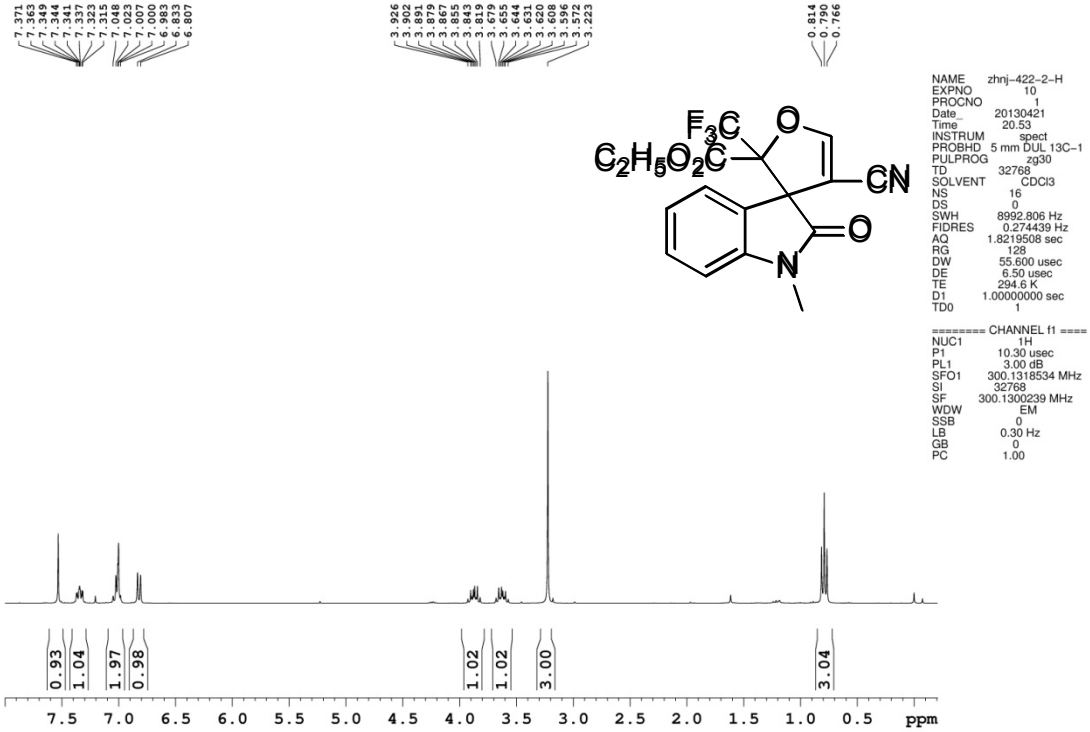

170.45
161.20
159.07
138.21
136.54
135.55
133.12
128.93
127.44
126.74
125.53
125.43
123.18
122.92
120.38
119.10
115.29
111.04
95.26
94.83
94.60
94.42
94.02
63.56
60.43
45.88
20.55
18.42
13.31
NAME zhnj-420-3-C
EXPNO 20
PROCNO 1
Date_ 20130422
Time 14.28
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 208
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 7298.2
DW 27.800 usec
DE 6.50 usec
TE 295.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

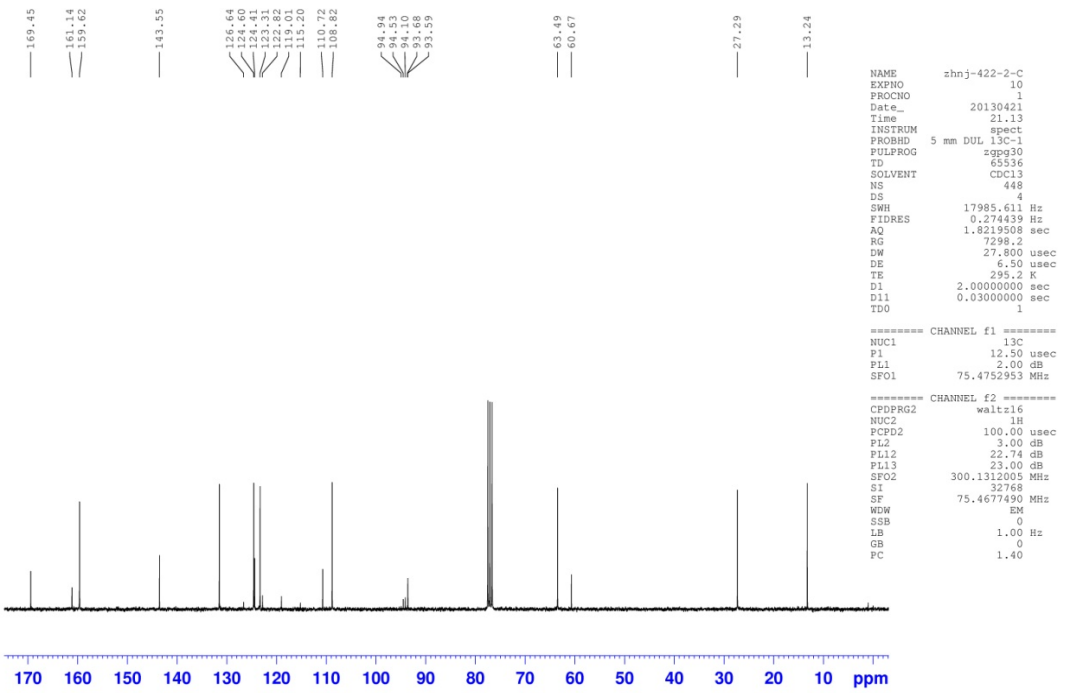

7.596
7.574
7.347
7.319
7.294
7.288
7.265
7.258
7.089
7.075
7.071
7.040
7.035
7.026
7.017
7.002
6.989
6.974
6.886
6.882
6.862
6.858
5.280
5.229
5.032
4.980
3.948
3.925
3.913
3.901
3.889
3.877
3.865
3.841
3.717
3.694
3.682
3.670
3.658
3.646
3.634
3.610
0.776
0.753
0.729
F3C
O
C2H5O2C
CN
O
N
Bn
F
NAME zhnj-421-3-H
EXPNO 10
PROCNO 1
Date_ 20130420
Time 10.22
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 90.5
DW 55.600 usec
DE 6.50 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300084 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.92
4.89
1.99
0.94
1.00
1.01
0.98
0.98
2.89
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

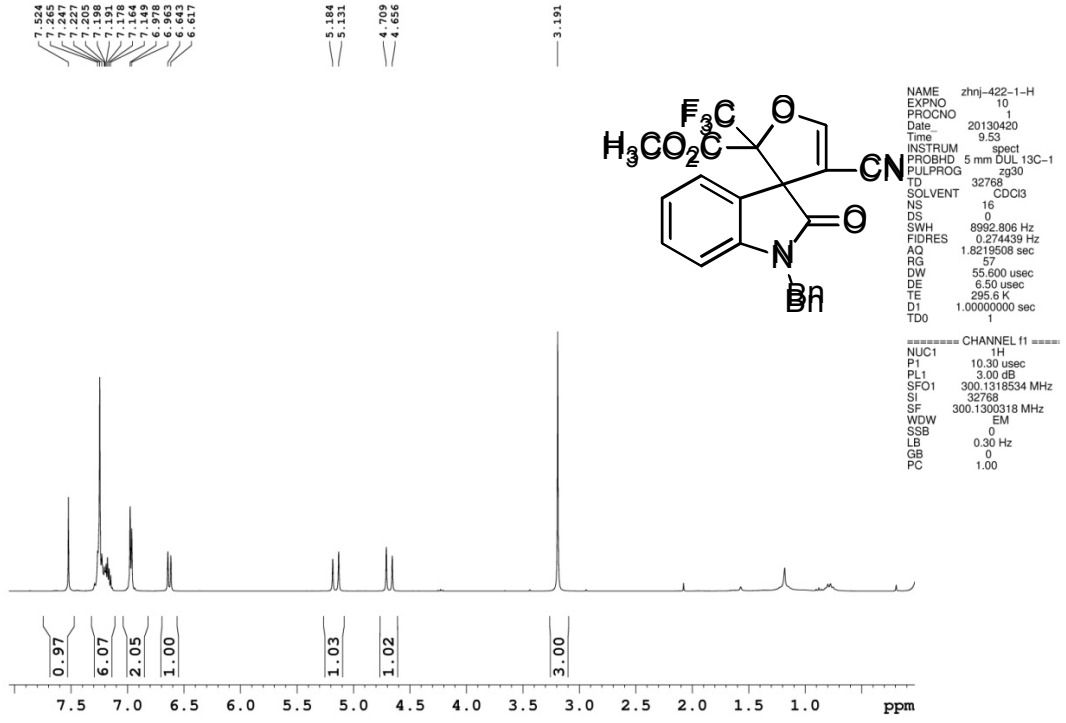

169.18
160.80
159.62
148.73
145.46
135.79
135.21
129.38
128.67
127.92
127.40
127.35
127.10
126.59
124.24
124.16
122.77
120.59
120.54
119.45
119.39
118.95
115.12
110.52
95.09
94.67
94.24
93.94
93.82
63.66
60.76
60.73
46.33
46.27
13.12
NAME zhnj-421-3-C
EXPNO 10
PROCNO 1
Date_ 20130420
Time 10.28
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 569
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 645.1
DW 27.800 usec
DE 6.50 usec
TE 296.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

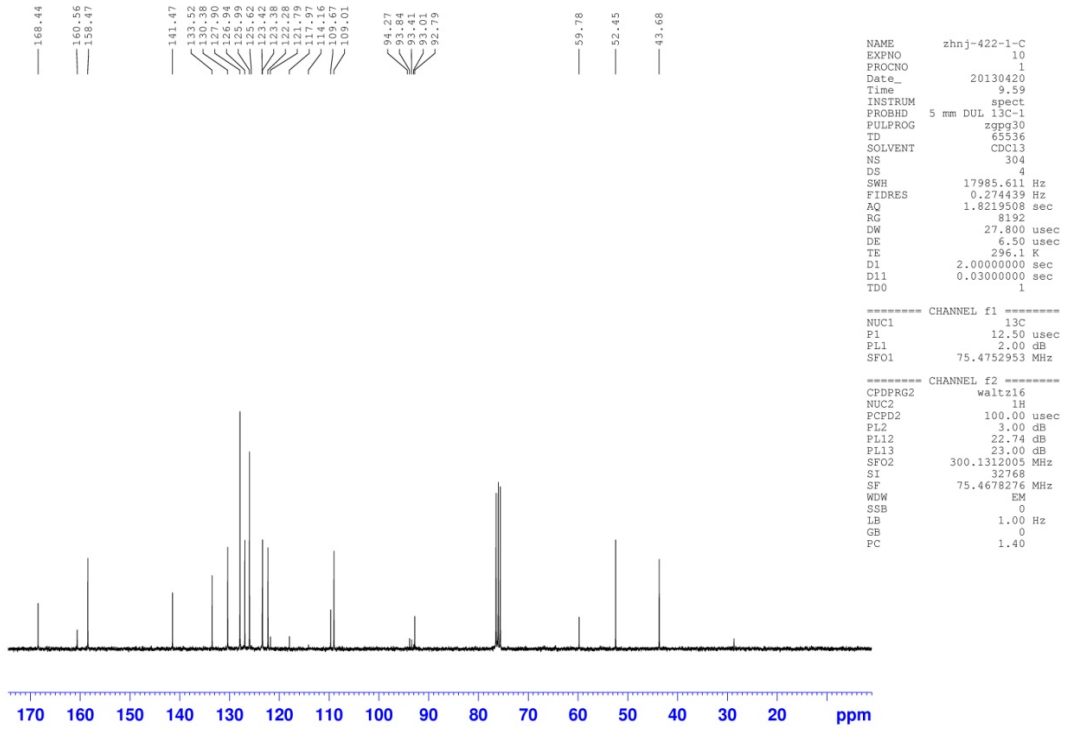

7.609 7.480 7.476 7.453 7.449 7.347 7.341 7.318 7.300 7.272 7.257 7.247 7.232 7.052 7.048 7.027 7.023 6.971 6.944 6.919
5.542 5.486 5.463 5.407
4.031 4.007 3.995 3.983 3.971 3.959 3.947 3.923 3.807 3.783 3.771 3.759 3.747 3.735 3.723 3.699
0.932 0.908 0.884
F3C
O
C2H5O2C
CN
O
N
Bn
Br
NAME zhnj-419-4-H
EXPNO 10
PROCNO 1
Date_ 20130415
Time 22.49
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 128
DW 55.600 usec
DE 6.50 usec
TE 294.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.86 0.93 4.70 0.91 0.95 0.92 1.00 0.93 0.94 2.87
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

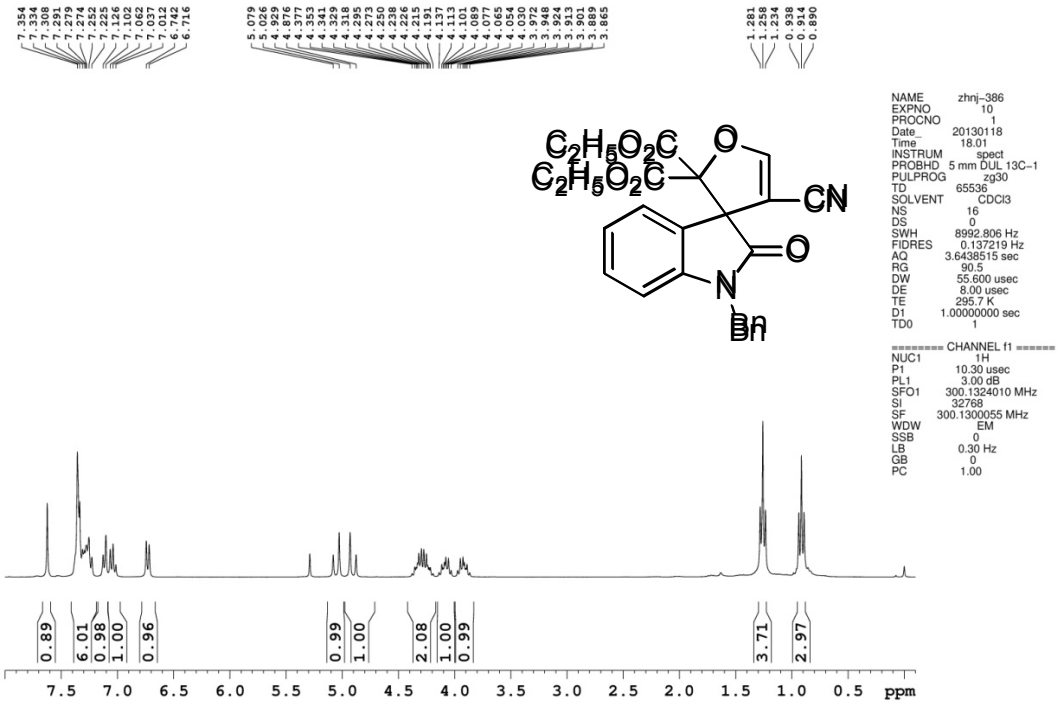

170.25
160.82 159.62
140.39 137.76 136.15 128.65 127.80 127.39 126.54 126.12 124.53 123.82 122.69 118.86 115.01 110.54
103.02
95.22 94.80 94.38 94.00
63.86 60.30
45.61
13.37
NAME zhnj-419-4-C
EXPNO 40
PROCNO 1
Date_ 20130416
Time 14.06
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 301
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 11585.2
DW 27.800 usec
DE 6.50 usec
TE 294.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

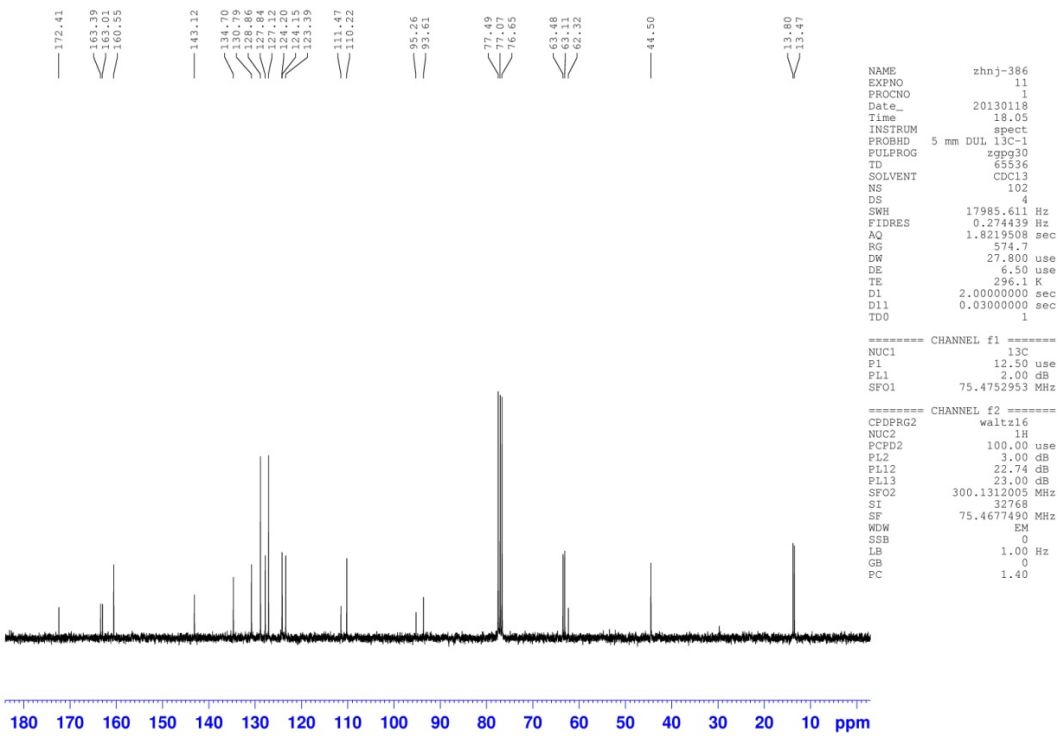

7.371
7.365
7.349
7.344
7.341
7.337
7.323
7.315
7.048
7.023
7.007
7.000
6.983
6.833
6.807
3.926
3.902
3.891
3.879
3.867
3.855
3.843
3.819
3.679
3.655
3.644
3.631
3.620
3.608
3.596
3.572
3.223
0.814
0.790
0.766
F3C
O
C2H5O2C
CN
O
N
NAME zhnj-422-2-H
EXPNO 10
PROCNO 1
Date_ 20130421
Time 20.53
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 128
DW 55.600 usec
DE 6.50 usec
TE 294.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300239 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.93
1.04
1.97
0.98
1.02
1.02
3.00
3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

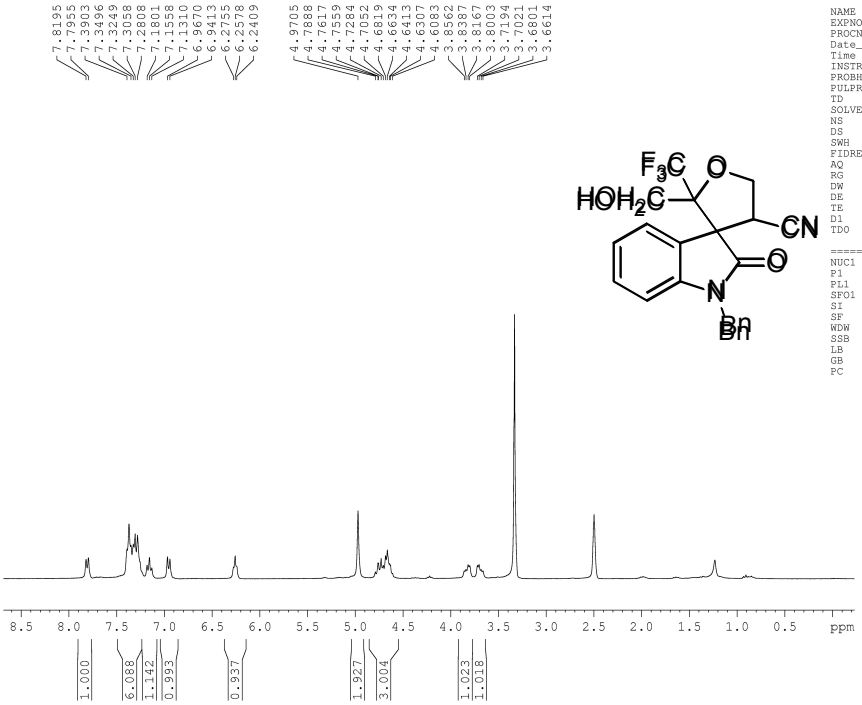

169.45
161.14
159.62
143.55
126.64
124.60
124.41
123.31
122.82
119.01
115.20
110.72
108.82
94.94
94.53
94.10
93.68
93.59
63.49
60.67
27.29
13.24
NAME zhnj-422-2-C
EXPNO 10
PROCNO 1
Date_ 20130421
Time 21.13
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 448
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 7298.2
DW 27.800 usec
DE 6.50 usec
TE 295.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.524
7.265
7.247
7.227
7.205
7.198
7.191
7.178
7.164
7.149
6.978
6.963
6.643
6.617
5.184
5.131
4.709
4.656
3.191
F3C
O
H3CO2C
CN
O
N
Bn
NAME zhnj-422-1-H
EXPNO 10
PROCNO 1
Date_ 20130420
Time 9.53
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 57
DW 55.600 usec
DE 6.50 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300318 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.97
6.07
2.05
1.00
1.03
1.02
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


168.44
160.56
158.47
141.47
133.52
130.38
127.90
126.94
125.99
125.62
123.42
122.88
122.28
121.79
117.97
114.16
109.67
109.01
84.27
83.84
93.41
93.01
92.79
59.78
52.45
43.68
NAME zhnj-422-1-C
EXPNO 10
PROCNO 1
Date_ 20130420
Time 9.59
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 304
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 8192
DW 27.800 usec
DE 6.50 usec
TE 296.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4678276 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

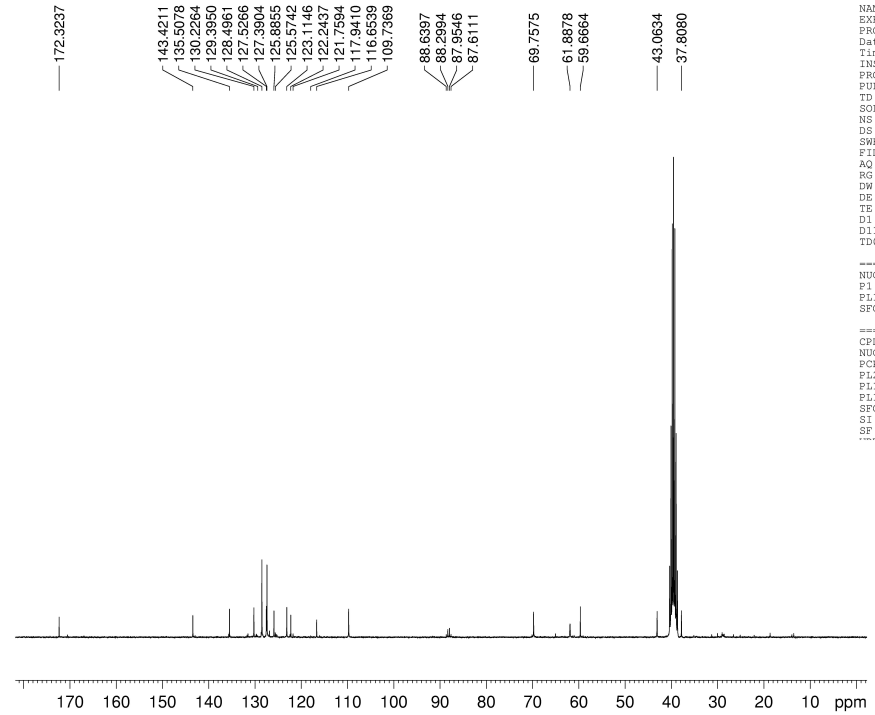

7.354
7.334
7.308
7.291
7.279
7.274
7.252
7.225
7.156
7.102
7.062
7.037
7.012
6.742
6.716
5.079
5.026
4.929
4.876
4.377
4.353
4.341
4.329
4.318
4.295
4.273
4.250
4.238
4.226
4.215
4.191
4.137
4.113
4.101
4.089
4.077
4.065
4.054
4.030
3.972
3.948
3.924
3.913
3.901
3.889
3.865
1.281
1.258
1.234
0.938
0.914
0.890
C2H5O2C
C2H5O2C
O
CN
O
N
Bn
NAME zhnj-386
EXPNO 10
PROCNO 1
Date_ 20130118
Time 18.01
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 90.5
DW 55.600 usec
DE 8.00 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 10.30 usec
PL1 3.00 dB
SFO1 300.1324010 MHz
SI 32768
SF 300.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.89
6.01
0.98
1.00
0.96
0.99
1.00
2.08
1.00
0.99
3.71
2.97
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


172.41
163.39
163.01
160.55
143.12
134.70
130.79
128.86
127.84
127.12
124.20
124.15
123.39
111.47
110.22
95.26
93.61
77.49
77.07
76.65
63.48
63.11
62.32
44.50
13.80
13.47
NAME zhnj-386
EXPNO 11
PROCNO 1
Date_ 20130118
Time 18.05
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 102
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 574.7
DW 27.800 use
DE 6.50 use
TE 296.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 =======
NUC1 13C
P1 12.50 use
PL1 2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 use
PL2 3.00 dB
PL12 22.74 dB
PL13 23.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm




```
NAME            zhnj20130916
EXPNO                     10
PROCNO                     1
Date_               20130916
Time                   14.06
INSTRUM                spect
PROBHD   5 mm DUL 13C-1
PULPROG                zg30
TD                    32768
SOLVENT                DMSO
NS                       16
DS                        0
SWH                8992.806 Hz
FIDRES                0.274439 Hz
AQ                 1.8219508 sec
RG                      256
DW                   55.600 usec
DE                    6.50 usec
TE                   298.9 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.30 usec
PL1                     3.00 dB
SFO1             300.1318534 MHz
SI                       32768
SF               300.1300042 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

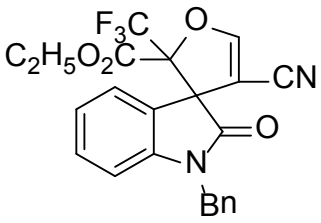


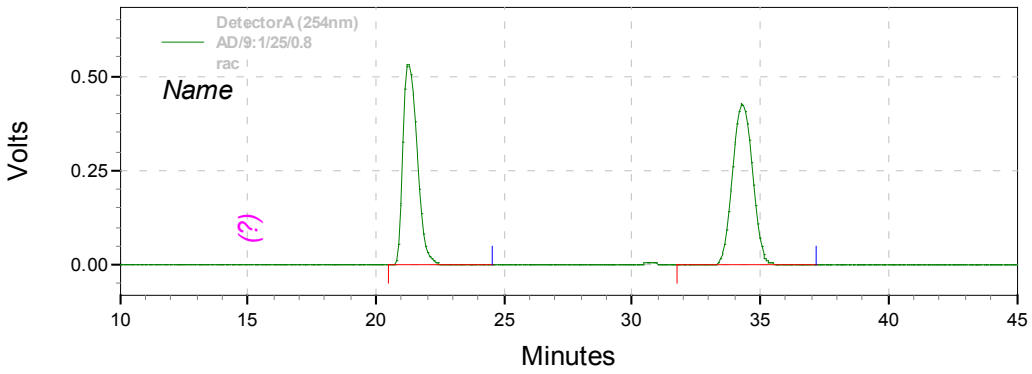

```
NAME            zhnj-20130918-2-C
EXPNO                     11
PROCNO                     1
Date_               20130918
Time                   22.50
INSTRUM                spect
PROBHD   5 mm DUL 13C-1
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                     9359
DS                        4
SWH               17985.611 Hz
FIDRES                0.274439 Hz
AQ                 1.8219508 sec
RG                     4597.6
DW                   27.800 usec
DE                    6.50 usec
TE                   299.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                    12.50 usec
PL1                    2.00 dB
SFO1             75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                    3.00 dB
PL12                  22.74 dB
PL13                  23.00 dB
SFO2             300.1312005 MHz
SI                       32768
SF               75.4677867 MHz
```

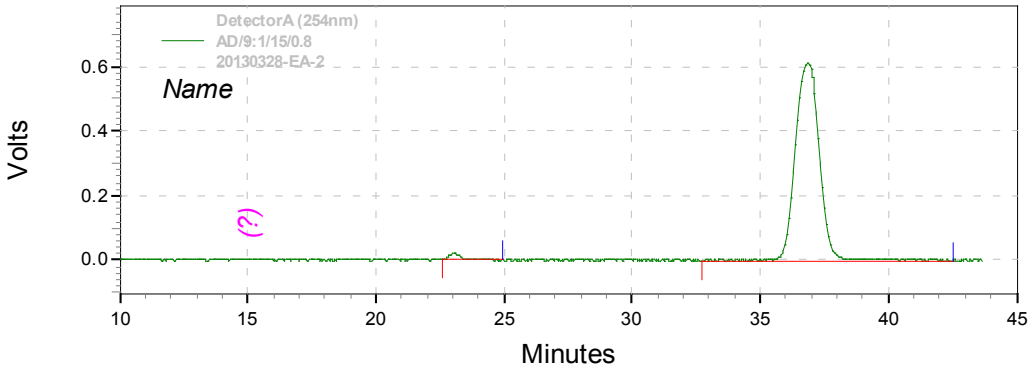
10. Chiral HPLC chromatography





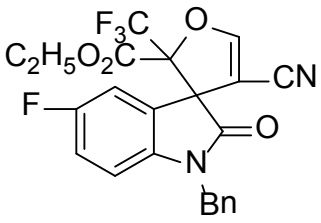
DetectorA (254nm)

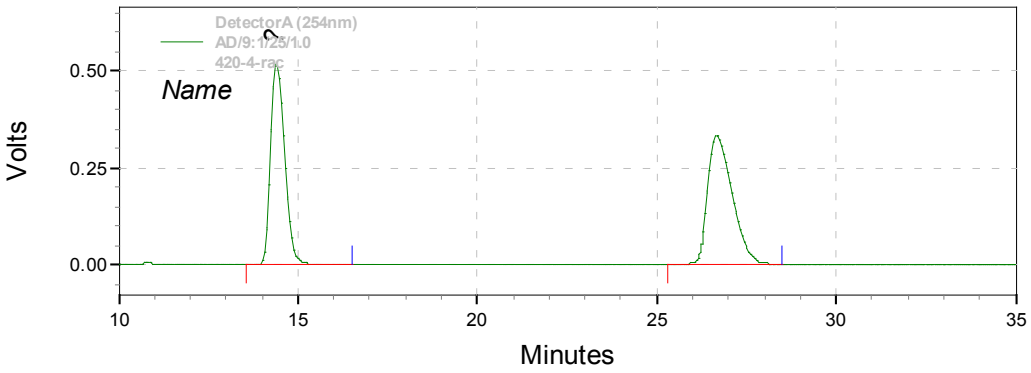
Pk #	Retention Time	Area	Area %
1	21.259	20710422	47.057
2	34.280	23300666	52.943



DetectorA (254nm)

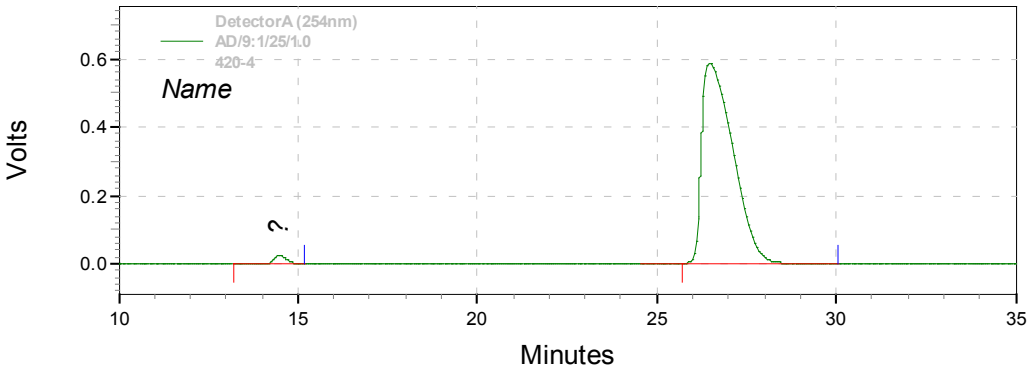
Pk #	Retention Time	Area	Area %
1	23.057	642117	1.594
2	36.841	39645486	98.406





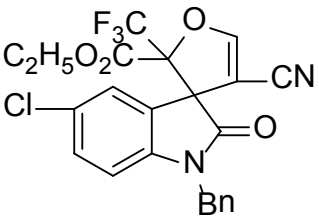
DetectorA (254nm)

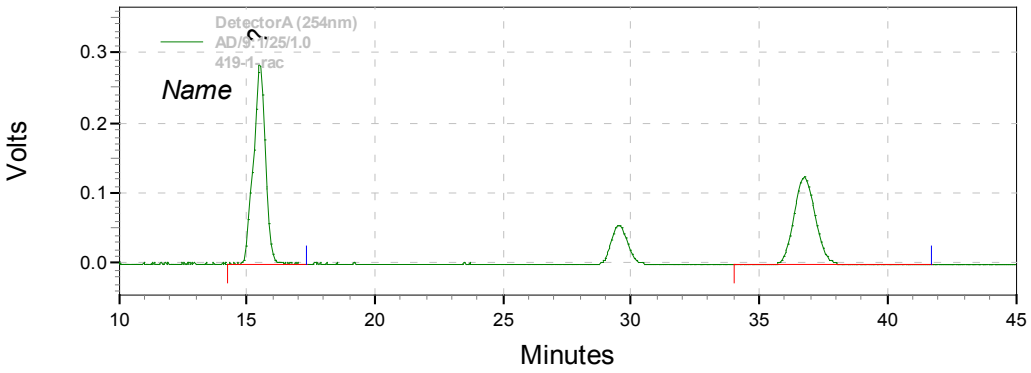
Pk #	Retention Time	Area	Area %
1	14.396	14063834	47.155
2	26.709	15761020	52.845



DetectorA (254nm)

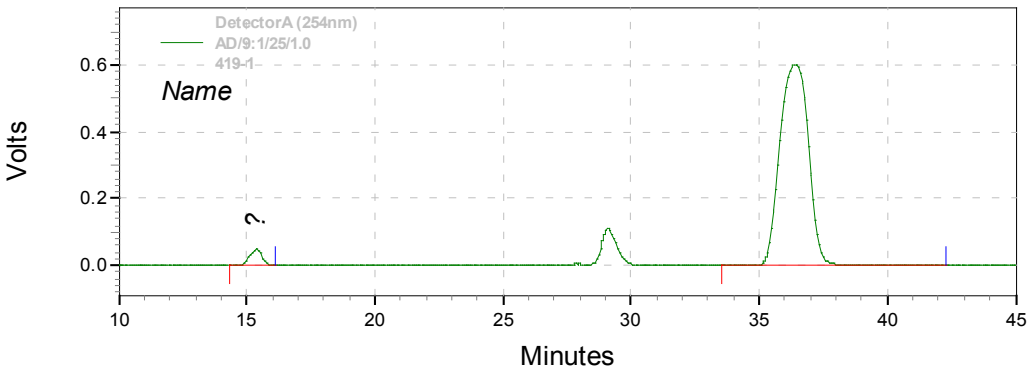
Pk #	Retention Time	Area	Area %
1	14.487	659955	1.801
2	26.509	35978687	98.199





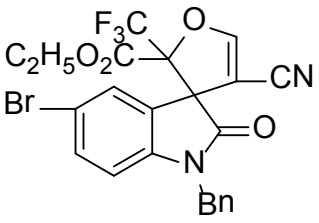
DetectorA (254nm)

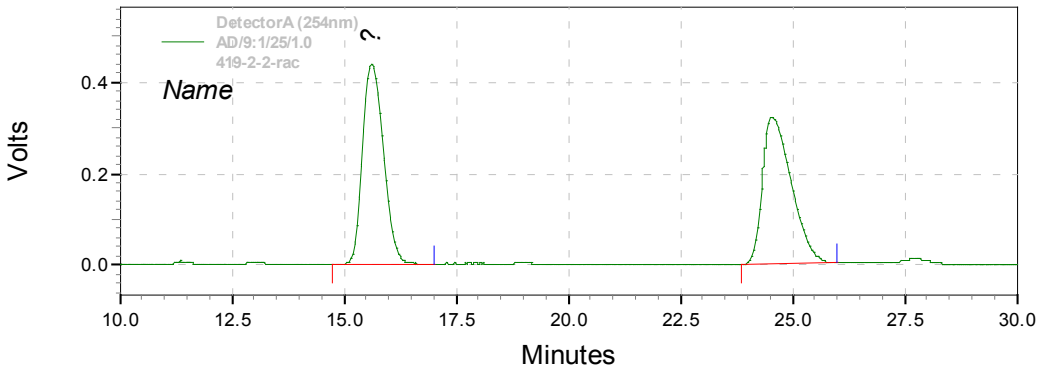
Pk #	Retention Time	Area	Area %
1	15.491	9153222	55.825
2	36.790	7243121	44.175



DetectorA (254nm)

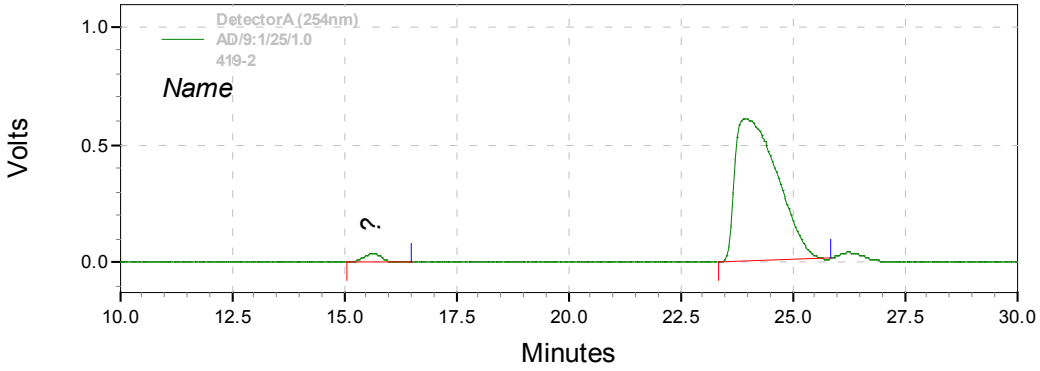
Pk #	Retention Time	Area	Area %
1	15.364	1647175	3.432
2	36.420	46349298	96.568





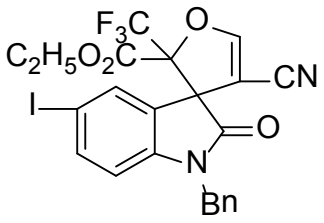
DetectorA (254nm)

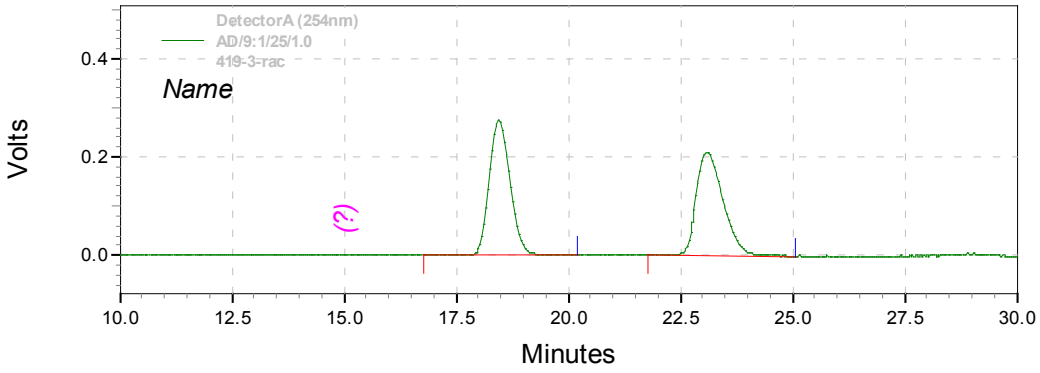
Pk #	Retention Time	Area	Area %
1	15.622	14003704	48.856
2	24.590	14659533	51.144



DetectorA (254nm)

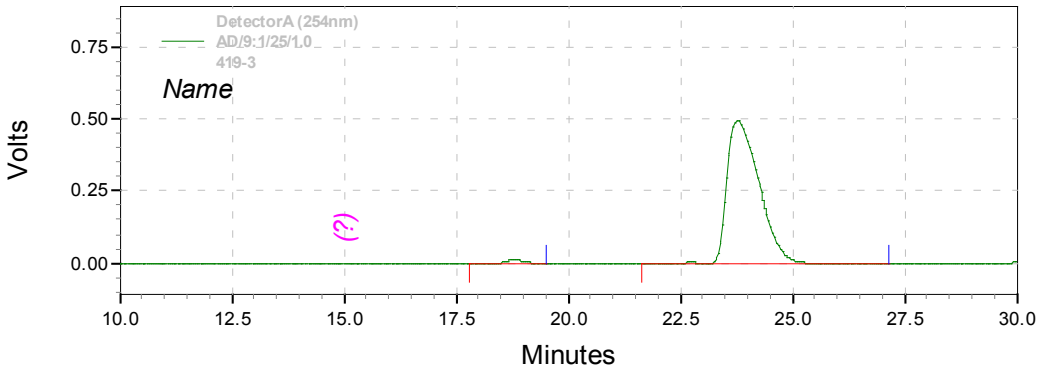
Pk #	Retention Time	Area	Area %
1	15.639	1038163	2.522
2	23.976	40132326	97.478





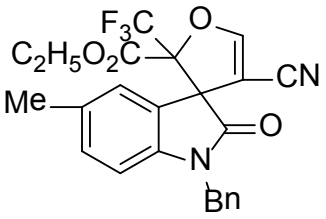
DetectorA (254nm)

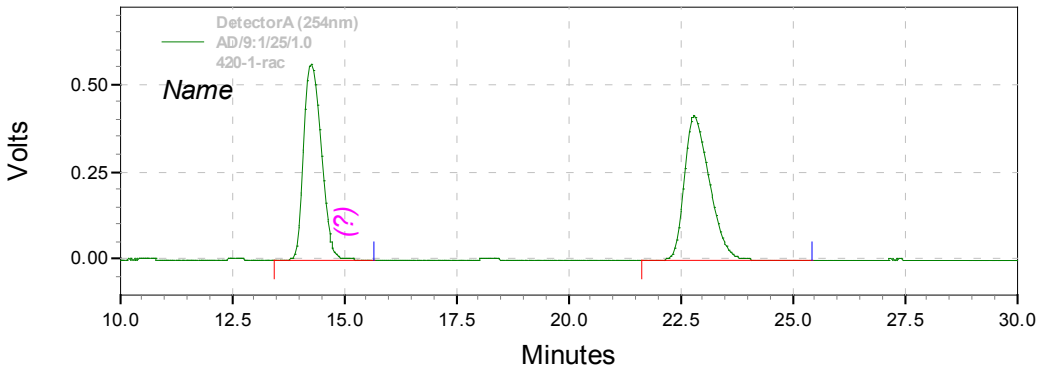
Pk #	Retention Time	Area	Area %
1	18.466	8751549	50.067
2	23.121	8728238	49.933



DetectorA (254nm)

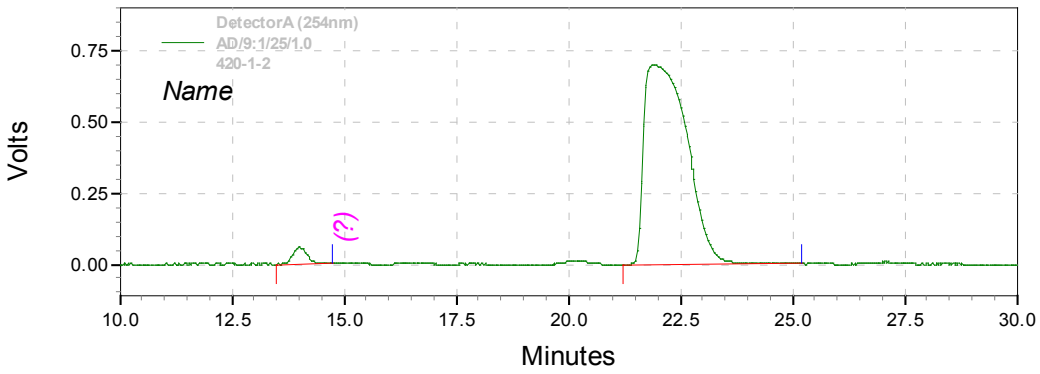
Pk #	Retention Time	Area	Area %
1	18.815	410304	1.609
2	23.792	25095076	98.391





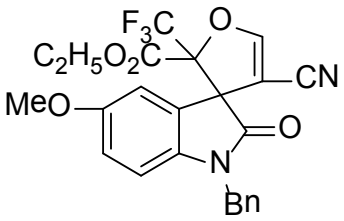
DetectorA (254nm)

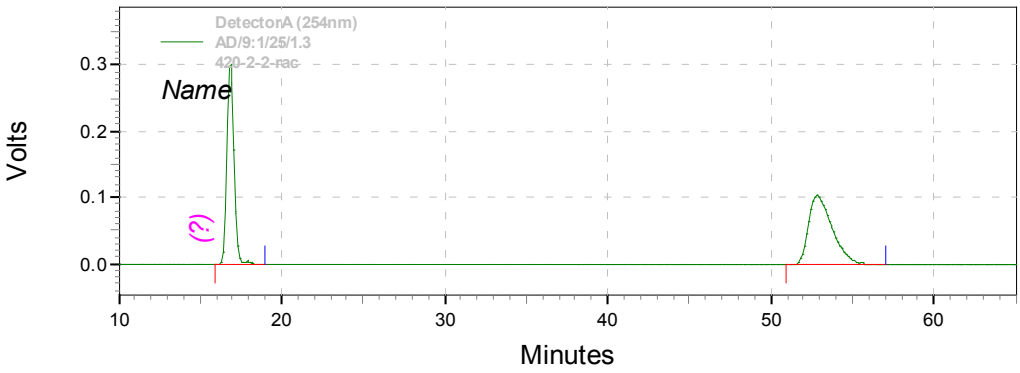
Pk #	Retention Time	Area	Area %
1	14.265	15111226	47.289
2	22.817	16844096	52.711



DetectorA (254nm)

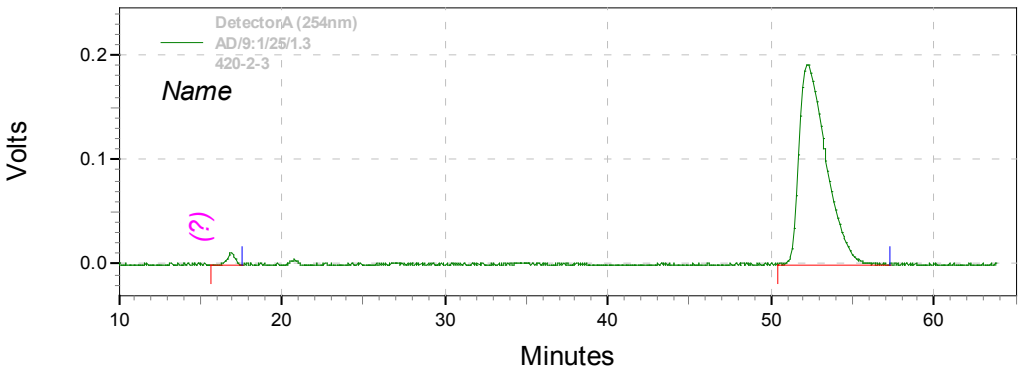
Pk #	Retention Time	Area	Area %
1	14.012	1275987	2.672
2	21.937	46476963	97.328





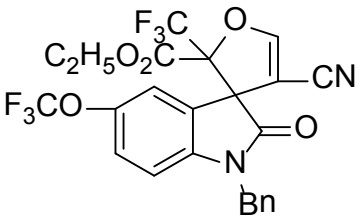
DetectorA (254nm)

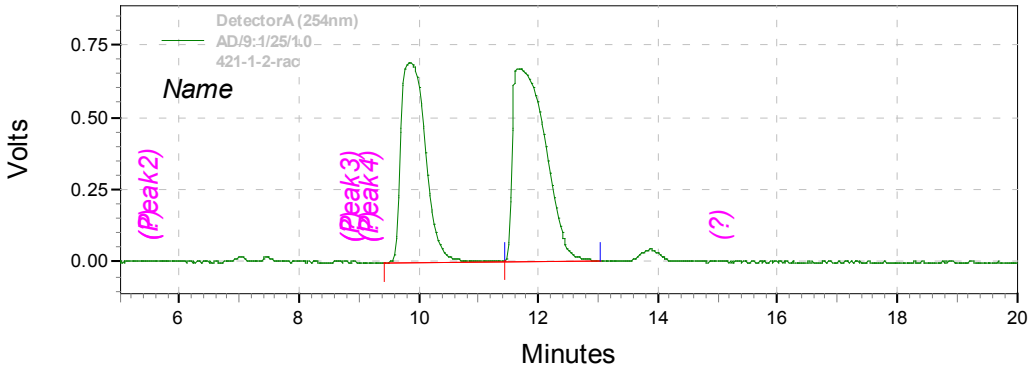
Pk #	Retention Time	Area	Area %
1	16.871	9155330	46.772
2	52.818	10418987	53.228



DetectorA (254nm)

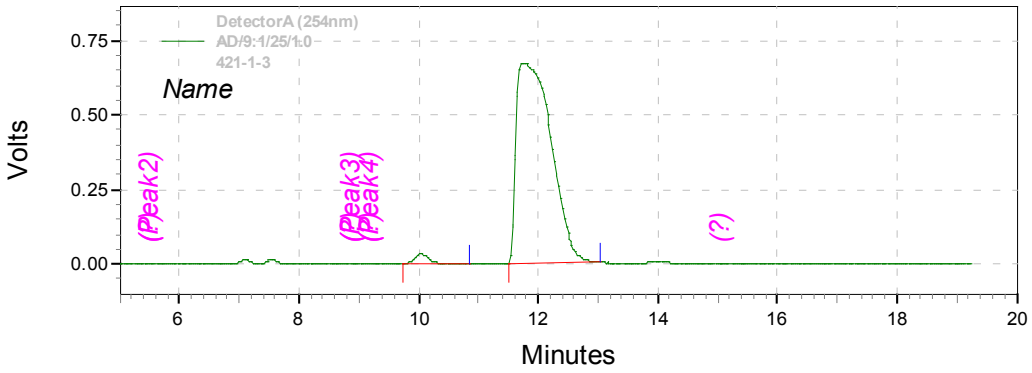
Pk #	Retention Time	Area	Area %
1	16.885	362247	1.619
2	52.252	22008355	98.381





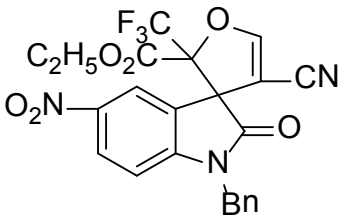
DetectorA (254nm)

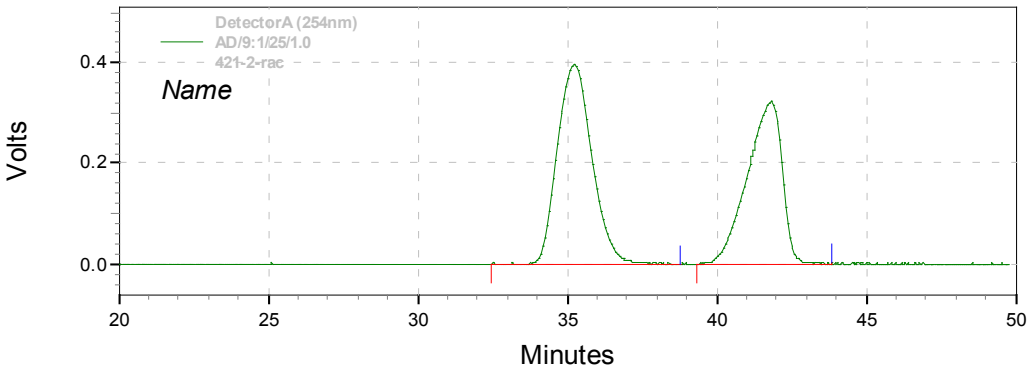
Pk #	Retention Time	Area	Area %
1	9.849	20165288	44.144
2	11.702	25515813	55.856



DetectorA (254nm)

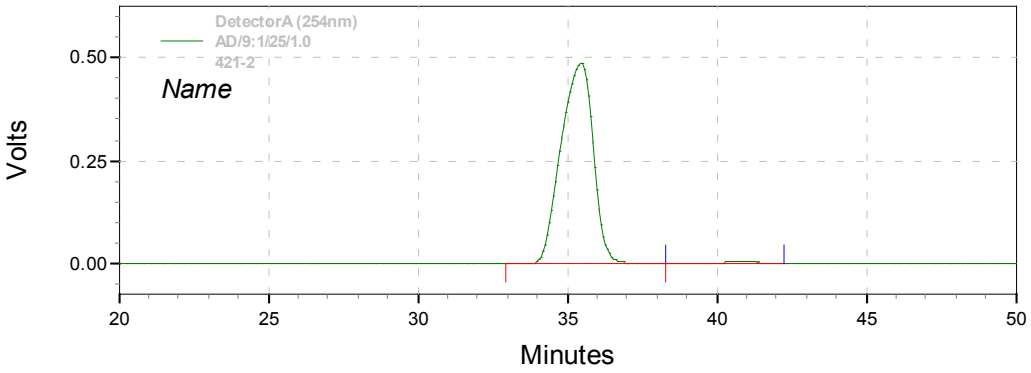
Pk #	Retention Time	Area	Area %
1	10.040	621220	2.229
2	11.771	27248217	97.771





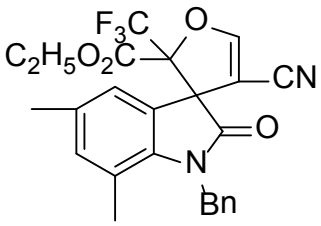
DetectorA (254nm)

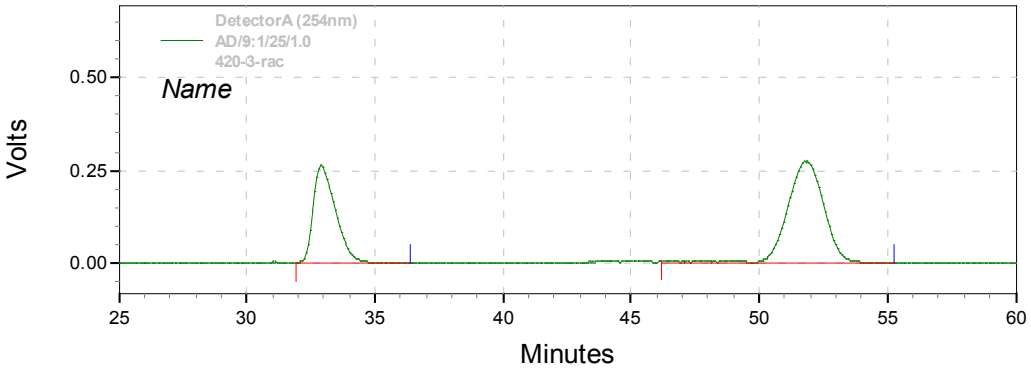
Pk #	Retention Time	Area	Area %
1	35.223	31360780	54.177
2	41.791	26524928	45.823



DetectorA (254nm)

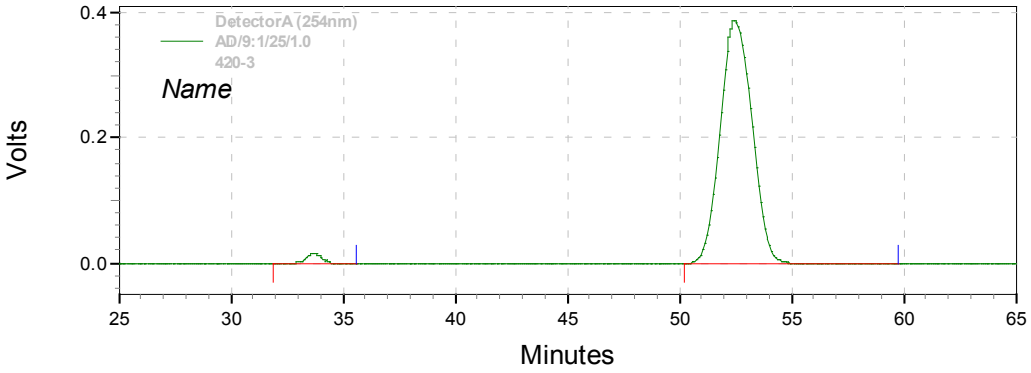
Pk #	Retention Time	Area	Area %
1	35.412	36099072	98.550
2	40.825	531230	1.450





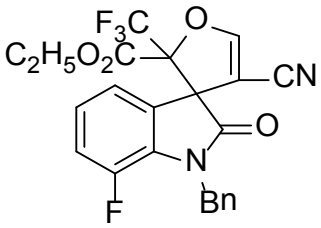
DetectorA (254nm)

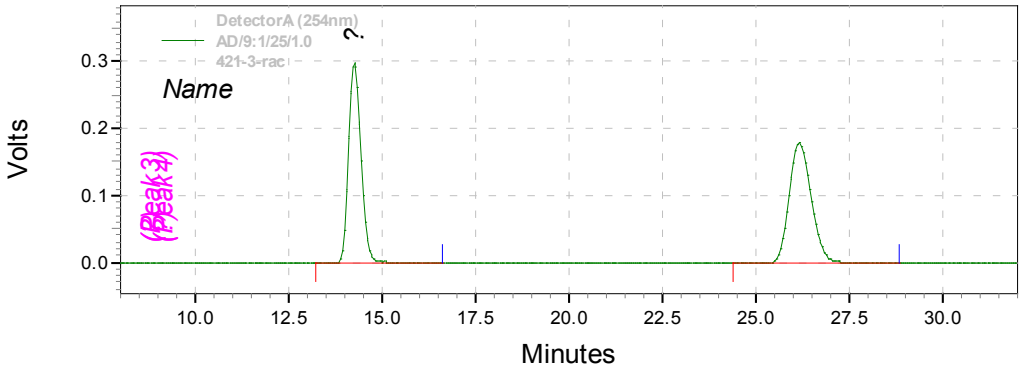
Pk #	Retention Time	Area	Area %
1	32.949	15424034	37.236
2	51.853	25998322	62.764



DetectorA (254nm)

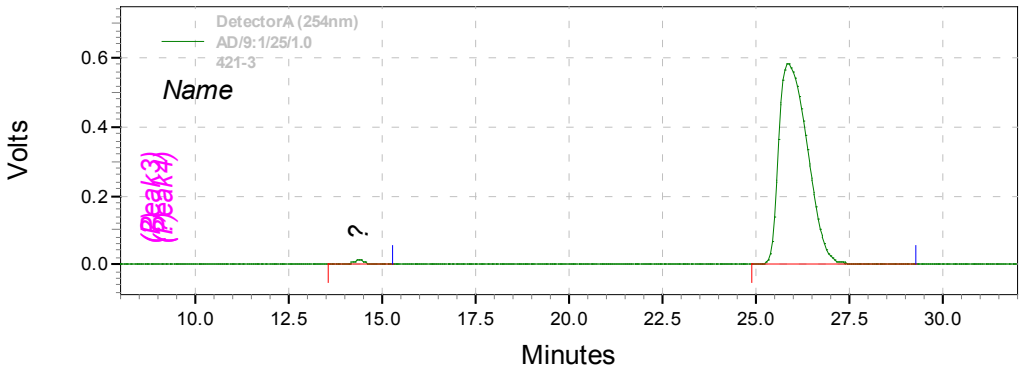
Pk #	Retention Time	Area	Area %
1	33.694	939431	2.277
2	52.512	40324784	97.723





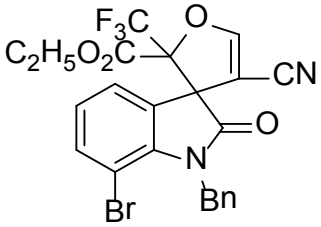
DetectorA (254nm)

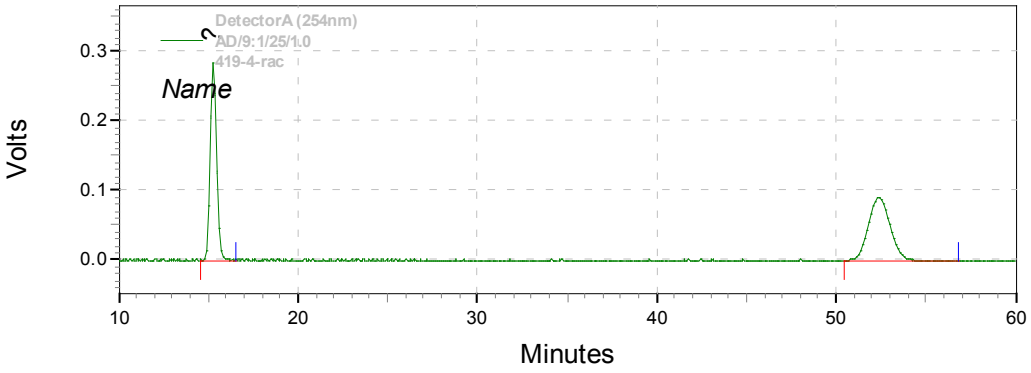
Pk #	Retention Time	Area	Area %
1	14.295	6963650	48.620
2	26.197	7359001	51.380



DetectorA (254nm)

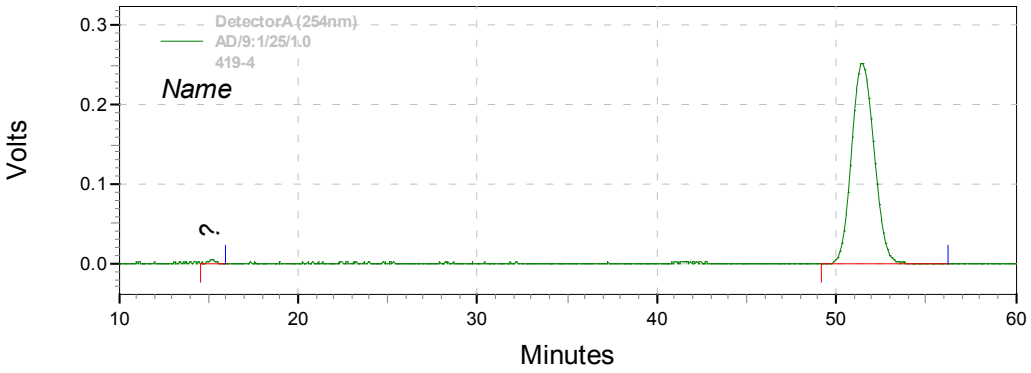
Pk #	Retention Time	Area	Area %
1	14.413	290622	0.932
2	25.926	30888422	99.068





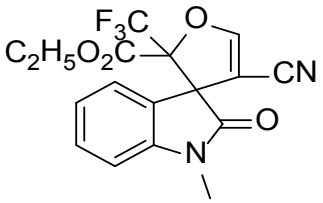
DetectorA (254nm)

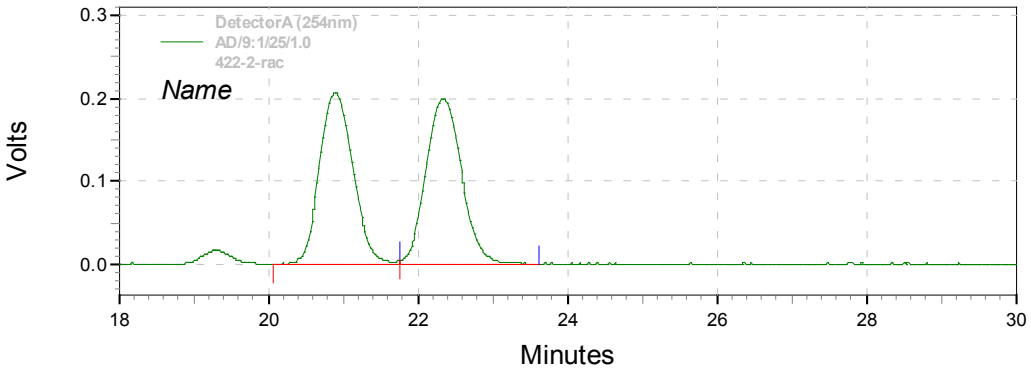
Pk #	Retention Time	Area	Area %
1	15.301	7055230	48.005
2	52.406	7641538	51.995



DetectorA (254nm)

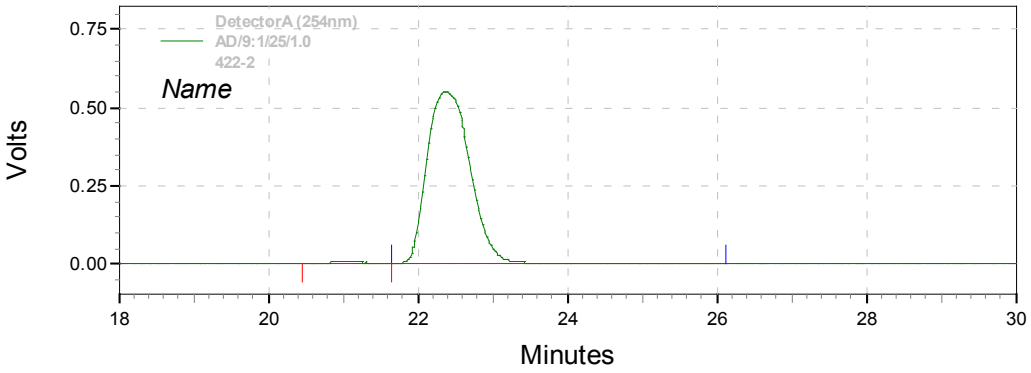
Pk #	Retention Time	Area	Area %
1	15.186	105613	0.475
2	51.479	22113888	99.525





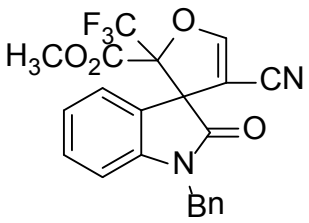
DetectorA (254nm)

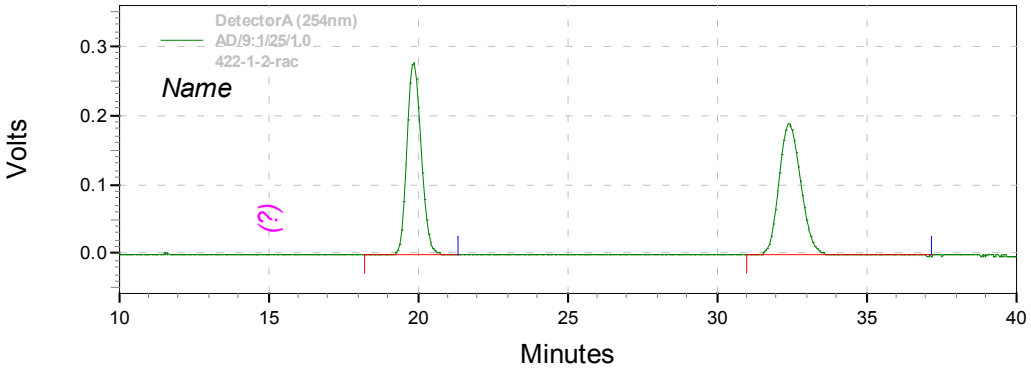
Pk #	Retention Time	Area	Area %
1	20.904	6413242	49.421
2	22.344	6563454	50.579



DetectorA (254nm)

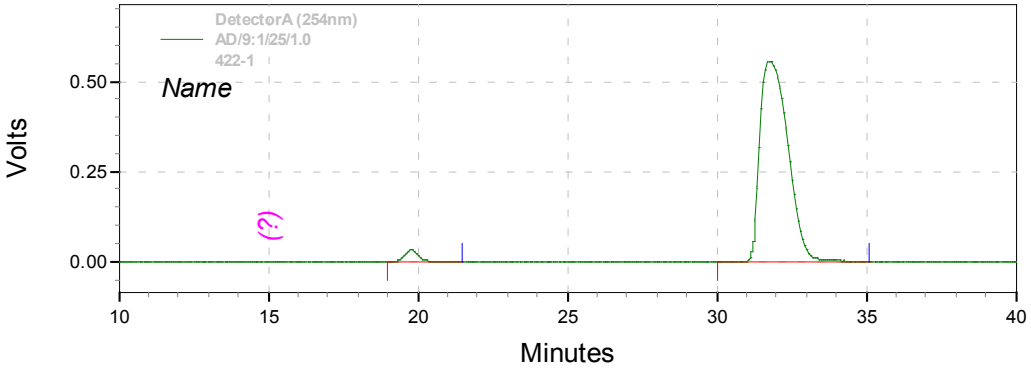
Pk #	Retention Time	Area	Area %
1	21.066	229702	1.031
2	22.389	22054054	98.969





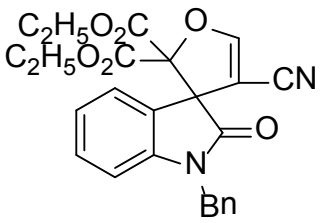
DetectorA (254nm)

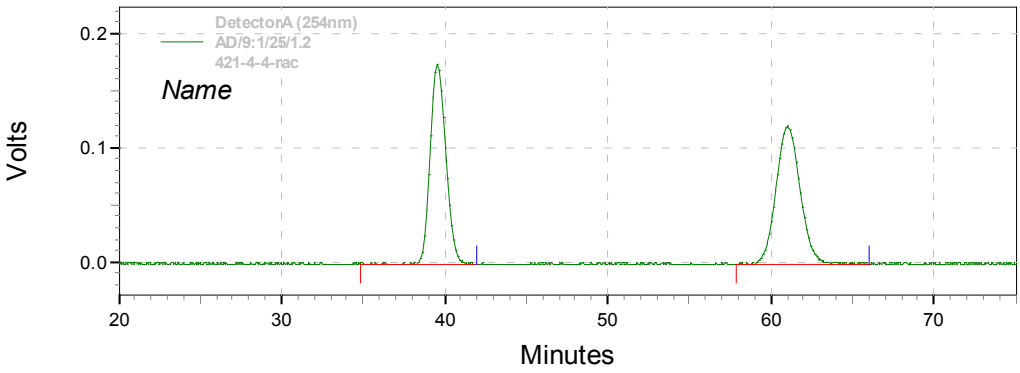
Pk #	Retention Time	Area	Area %
1	19.879	9092914	48.661
2	32.446	9593381	51.339



DetectorA (254nm)

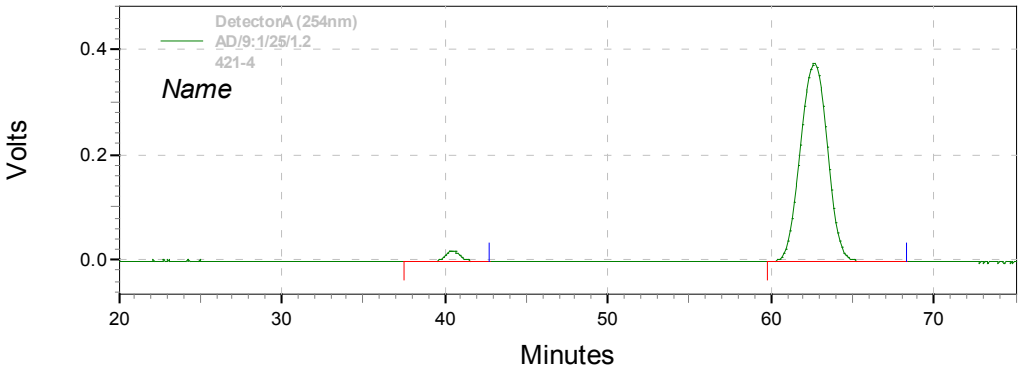
Pk #	Retention Time	Area	Area %
1	19.791	1015815	2.746
2	31.807	35970395	97.254





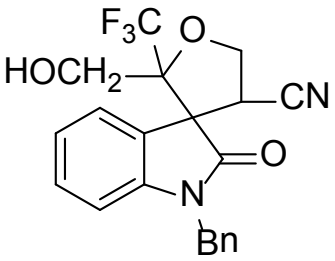
DetectorA (254nm)

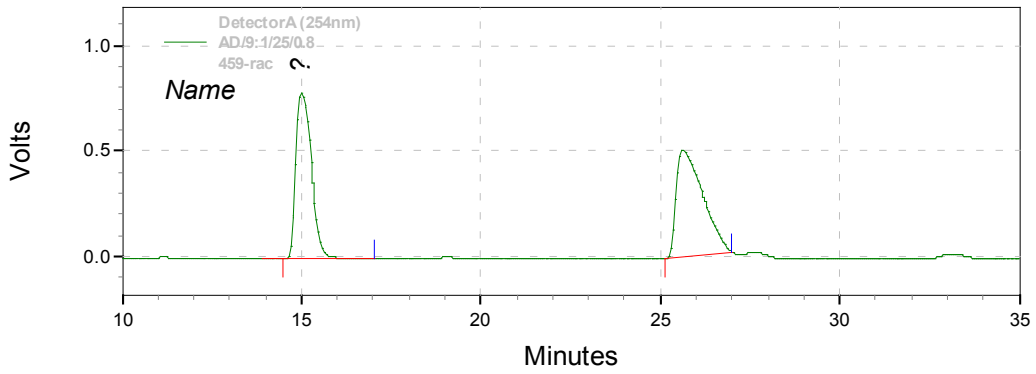
Pk #	Retention Time	Area	Area %
1	39.520	11641067	48.704
2	61.010	12260511	51.296



DetectorA (254nm)

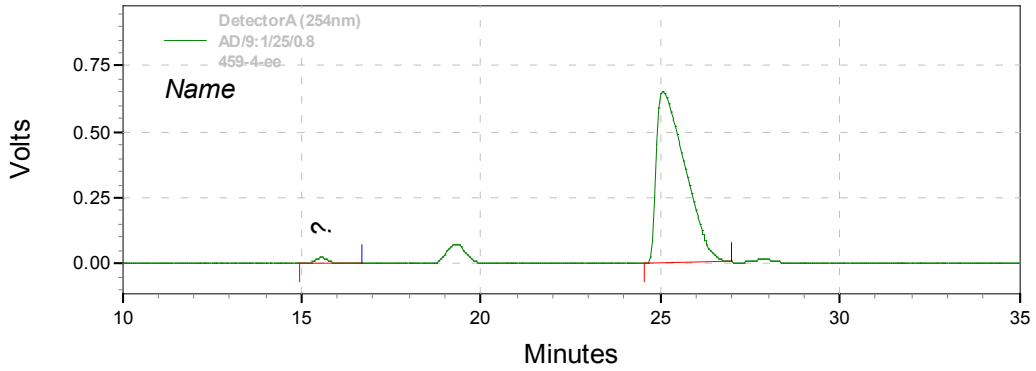
Pk #	Retention Time	Area	Area %
1	40.442	1365052	3.032
2	62.643	43651146	96.968





DetectorA (254nm)

Pk #	Retention Time	Area	Area %
1	14.983	24583016	48.296
2	25.611	26317305	51.704



DetectorA (254nm)

Pk #	Retention Time	Area	Area %
1	15.584	665328	1.826
2	25.066	35772110	98.174